N-CONTAINING LIGANDS AS UNIVERSAL COORDINATION ENVIRONMENTS FOR RARE-EARTH ALKYL AND BIS(ALKYL) COMPLEXES

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Abstract

This review summarizes recent advances in the chemistry of σ-hydrocarbyl rare-earth metal complexes stabilized by nitrogen-containing ligands with main emphasis on the synthesis, structural features, stability, and reactivity of these compounds.

Key words: rare-earth metals, alkyl complexes, ligands, synthesis.
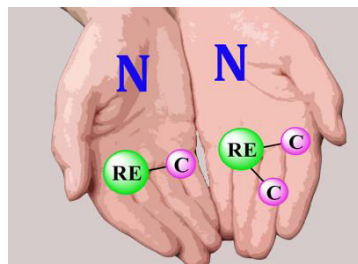
1. Introduction

Past decades have seen an impressive progress in the design and synthesis of new σ-bonded rare-earth metal alkyl complexes owing to their unique reactivity and the ability to promote various thermodynamically unfavorable reactions, including C−H bond activation and alkane functionalization [1–4]. Along with the high reactivity in stoichiometric reactions, rare-earth hydrocarbyl complexes hold great promise for catalysis of a wide range of transformations involving unsaturated substrates, such as polymerization (alkenes, dienes, and lactides) [5–11] hydrogenation [12–13], hydrosilylation [14], hydroamination [15–18], hydrophosphination (alkenes and alkynes) [19–22], hydroboration (alkenes) [23, 24], and alkyne dimerization [25, 26].

Owing to the large ionic radii, the Lewis acidity, and the presence of unoccupied 5d and 6s orbitals (for the Ln^{3+} ions) [27], rare-earth elements show a pronounced tendency to form complexes and acquire high coordination numbers. An insignificant contribution of the covalent component to the rare-earth metal–ligand interactions removes restrictions associated with the compatibility of orbitals in symmetry. This can give rise to radically new types of compounds the reactivity of which differs from that of d-element derivatives. A similarity in the redox [28] and chemical properties of rare-earth elements along with a substantial variation of the ionic radii within a series of their compounds (Sc^{3+} 72.3 pm, Y^{3+} 89.3 pm, La^{3+} 101.6 pm, Nd^{3+} 99.5 pm, Eu^{3+} 95.1 pm, Lu^{3+} 85.0 pm) [27] offer a unique possibility of optimizing the reactivity of metal complexes by designing a metal coordination sphere and choosing an appropriate radius of the central atom in accordance with the main features of the catalyzed reaction.
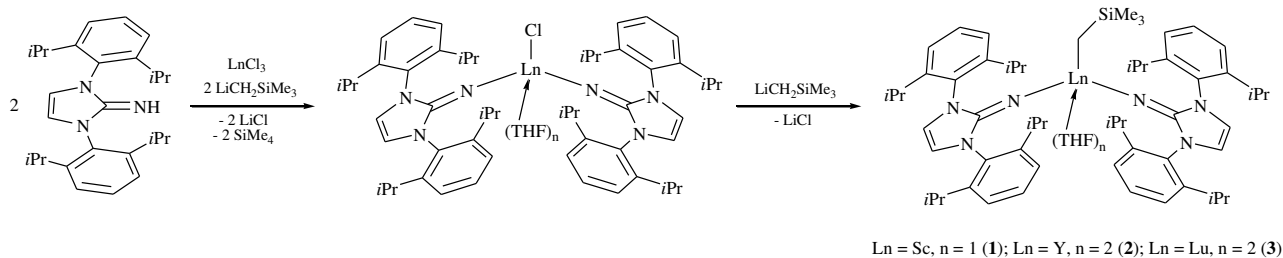
In recent years, there has been a trend towards the design of new non-cyclopentadienyl ligand systems that allow for stabilization of rare-earth metal alkyl and hydride complexes

[29, 30]. The main objectives of the ligand replacement are to enhance the stability of rare-earth metal derivatives with the maintenance of their high catalytic activity, to increase the catalyst tolerance to functional groups of substrates, to extend the scope of the design and fine-tuning of the geometry of a metal coordination sphere in the resulting complexes, and to control the catalytic activity of rare-earth element compounds and the selectivity of metal-promoted reactions [31, 32]. Of particular interest is the investigation of the effect of a coordination environment of rare-earth metal atoms on the reactivity of the M–C and M–H bonds and the catalytic activity of their compounds. It should also be noted that nitrogen-containing ligand systems are widely used in the chemistry of organic derivatives of lanthanides, since they offer multiple synthetic solutions to the problem of modification of the electronic and steric properties [33].
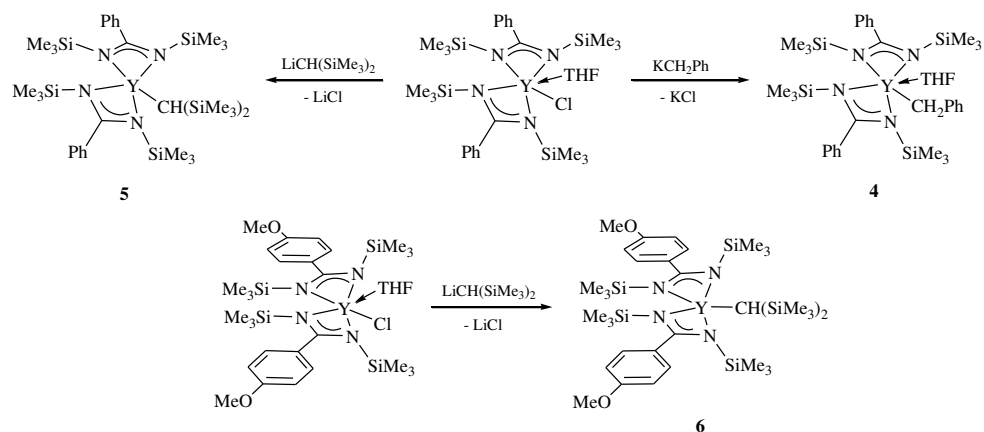
2.1. Rare-earth monoalkyl complexes with the monodentate *N*-containing ligands

Imidazoline-2-imine ligands (Im^RN) have been successfully used in the chemistry of organic derivatives of rare-earth elements as effective coordination environments that are able to stabilize alkyl complexes [34].
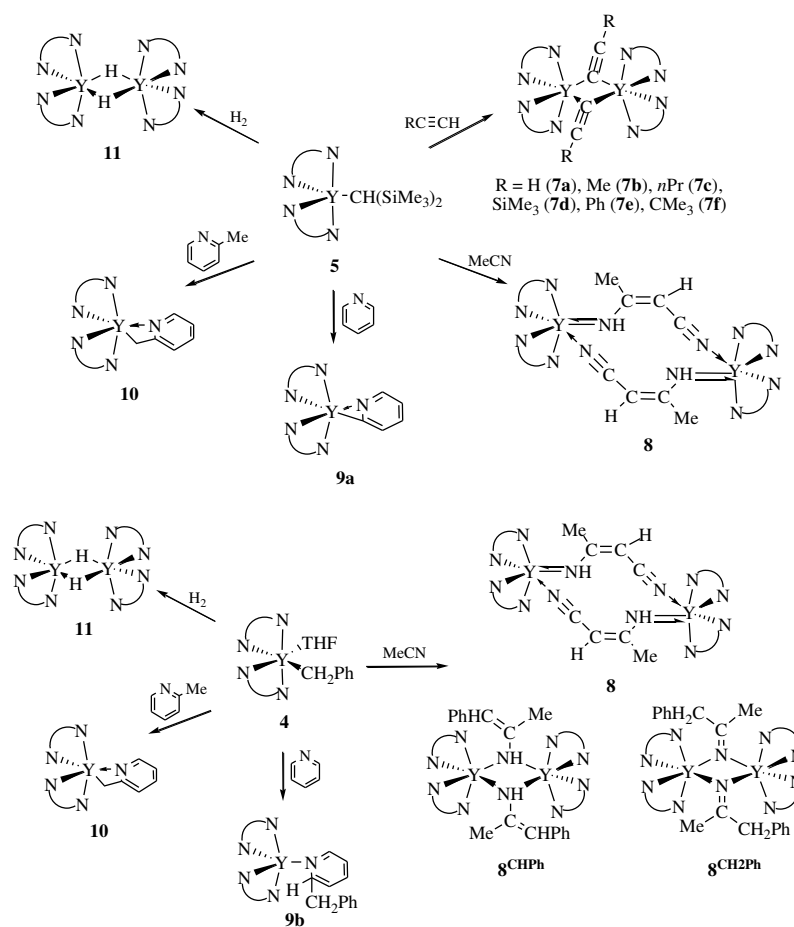
Chloride complexes of rare-earth elements $(Im^{Dipp}N)_2LnCl(THF)_n$ (Ln = Sc, n = 1 or 2; Ln = Y, n = 2; Ln = Lu, n = 2) were obtained by the treatment of 1,3-bis(2,6-diisopropylphenyl)imidazolyl-2-imine with two equivalents of $LiCH_2SiMe_3$ and one equivalent of anhydrous $LnCl_3$ (Ln = Y, Lu, Sc) (Scheme 1) [34]. The subsequent interaction with an equimolar amount of $LiCH_2SiMe_3$ in THF resulted in the corresponding alkyl bis(imine) derivatives $(Im^{Dipp}N)_2LnCH_2SiMe_3(THF)_n$ (Ln = Sc, n = 1 (**1**); Ln = Y, n = 2 (**2**); Ln = Lu, n = 2 (**3**)). According to the NMR spectroscopy data, scandium complex **1** contains one coordinated THF

Ln = Sc, n = 1 (**1**); Ln = Y, n = 2 (**2**); Ln = Lu, n = 2 (**3**)

Scheme 1

Scheme 2

R = H (**7a**), Me (**7b**), *n*Pr (**7c**), SiMe₃ (**7d**), Ph (**7e**), CMe₃ (**7f**)

Scheme 3

molecule, while similar compounds of yttrium and lutetium include two molecules of THF. The X-ray analyses indicated that alkyl compounds of Y (**2**) and Lu (**3**) are isostructural. The coordination environment of the central metal atom is a distorted trigonal bipyramid.

2.2. Rare-earth monoalkyl complexes with the bidentate *N*-containing ligands

Bidentate amidinate ligands $[RC(NR')_2]^-$ are one of the first non-cyclopentadienyl ligand systems that have been successfully used for the synthesis of alkyl complexes of rare-earth elements. In 1996 Teuben *et al.* synthesized a series of monomeric bis(amidinate) alkyl and benzyl derivatives of yttrium $[PhC(NSiMe_3)_2]_2YR(THF)_n$ (R = CH_2Ph, n = 1 (**4**); R = $CH(SiMe_3)_2$, n = 0 (**5**)) and [*p*-$MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**6**) (Scheme 2) [35].

Complexes **4**–**6** are thermally stable in C_6D_{12} or C_6D_6. Upon heating of their solutions at 100 °C for several hours, there were no signs of H/D exchange, solvent metalation or thermal decomposition. The XRD analysis of complex **6** showed that this compound is monomeric, and the steric demand of the amidinate moiety is comparable with that of the pentamethylcyclopentadienyl ligand. Based on the results of semi-empirical calculations using the INDO/1 method for model complexes $[HC(NH)_2]_2YMe$ and $(C_5H_5)_2YMe$, it was concluded that the high electron-withdrawing activity of the amidinate ligands leads to an increase in the positive charge on the yttrium atom in the bis(amidinate) derivatives compared to the analogs of a metallocene series. The charge separation in the Y–C bond in complex $[HC(NH)_2]_2YMe$ composed 1.06 e *vs* 0.75 e in $(C_5H_5)_2YMe$, which indicates a much higher bond polarity in the bis(amidinate) derivative. In the authors' opinion, the high value of the positive charge on the yttrium atom in $[HC(NH)_2]_2YMe$ leads to a greater orbital contraction, which complicates the interaction between the metal atom and the substrate, resulting in their inactivity in H/D exchange (for example, H_2), as well as reduces the rates of hydrogenolysis compared to those of the cyclopentadienyl compounds [35].

The dimeric acetylide complexes of a general formula $[L_2Y(\mu-C{\equiv}CR)]_2$ (R = H (**7a**), Me (**7b**), *n*Pr (**7c**), SiMe₃ (**7d**), Ph (**7e**), CMe₃ (**7f**)) were obtained by the σ-bond metathesis of compound **5** with terminal alkynes (Scheme 3). The reaction of acetonitrile with complex **5** gave rise to dimer $[L_2Y(\mu-(N,N')-N(H)C(Me)=C(H)C{\equiv}N)]_2$ **8**, whereas an analogous reaction with complex **4** afforded not only complex **8** but also the products of insertion of the multiple nitrogen–carbon bond: $[L_2Y(\mu-$

$N=C(Me)CH_2Ph)]_2$ (**8^{CH2Ph}**) and $[L_2Y(\mu-N(H)C(Me)=C(H)Ph)]_2$ (**8^{CHPh}**). The reaction of pyridine with compound **5** led to the metallation of the pyridine ring at the α-position with the formation of $L_2Y(C_5H_4N)$ (**9a**), while the same reaction with compound **4** afforded complex $L_2Y[C_5H_5(CH_2Ph)N]$ **9b** due to the addition of the benzyl group to the multiple bonds of the heterocycle. The reactions of alkyl (**5**) and benzyl (**4**) derivatives of yttrium with 2-methylpyridine were accompanied by the activation of the C–H bond of the methyl groups and led to heterobenzyl derivative $L_2Y(o-CH_2C_5H_4N)$ (**10**) (Scheme 3). Dimeric hydride complex with a benzamidinate ligand $\{[PhC(NSiMe_3)_2]_2Y(\mu-H)\}_2$ (**11**) was obtained by the hydrogenation of both compounds $[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**5**) and $[PhC(NSiMe_3)_2]_2YCH_2Ph$ (**4**) with H_2 (3 atm) in benzene at 40 °C. Complex **11** was the first one and remained for a long time the only one rare-earth hydride derivative stabilized by the non-cyclopentadienyl ligand system [36, 37]. Compound **11** demonstrated high stability in hydrocarbon solvents upon heating to 100 °C but reacted with the C–O bond of THF. Treatment of complex **11** with acetonitrile and pyridine resulted in $\{[PhC(NSiMe_3)_2]_2Y(\mu-N=C(H)Me)\}_2$ and $[PhC(NSiMe_3)_2]_2Y(NC_5H_6)$, respectively. Dimeric acetylide complex $\{[PhC(NSiMe_3)_2]_2Y(\mu-C{\equiv}CH)\}_2$ (**7a**) was obtained by the reaction of **11** with acetylene.

Alkyl and aryl scandium species with amidinate ligands $[PhC(NSiMe_3)_2]_2ScR$ (R = CH_2SiMe_3 (**12**), Mes (**13**)) and $[PhC(NSiMe_3)_2]_2ScMe(THF)$ (**14**) were obtained by the metathesis reactions between the corresponding chloride compound $[PhC(NSiMe_3)_2]_2ScCl(THF)$ and alkyllithium reagents (Scheme 4) [38]. The reaction of compound **12** with $Me_3SiC{\equiv}CH$ resulted in monomeric acetylenide complex $[PhC(NSiMe_3)_2]_2Sc(C{\equiv}CSiMe_3)$ (**15**). Dimeric hydride complex $\{[PhC(NSiMe_3)_2]_2Sc(\mu-H)\}_2$ (**16**) was isolated in high yield upon hydrogenation of derivative **12** with H_2. Complex **16** is stable in a solution of C_6D_6: no signs of decomposition were detected even after heating at 60 °C for a day. Treatment of complex **16** with D_2 did not lead to H/D exchange. Furthermore, the dimeric structure of hydride complex **16** was preserved even upon treatment with THF. The addition of **16** across the triple C≡C bond of tolane led to the formation of complex $[PhC(NSiMe_3)_2]_2ScC(Ph)=C(Ph)H$.

The reactions of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Er, Dy, Sm) with two equivalents of bulky formamidines 2,6-$(Me)_2C_6H_3N=CH=NHC_6H_3(Me)_2$-2,6 (HL^1) and 2,6-$(iPr)_2C_6H_3N=CH=NHC_6H_3(iPr)_2$-2,6 (HL^2) in hexane at 0 °C

Scheme 4

R = *i*Pr (**22**)

R = Me, Ln = Y (**17**);
R = *i*Pr: Ln = Y (**18**),
Sm (**19**), Er (**20**), Dy (**21**)
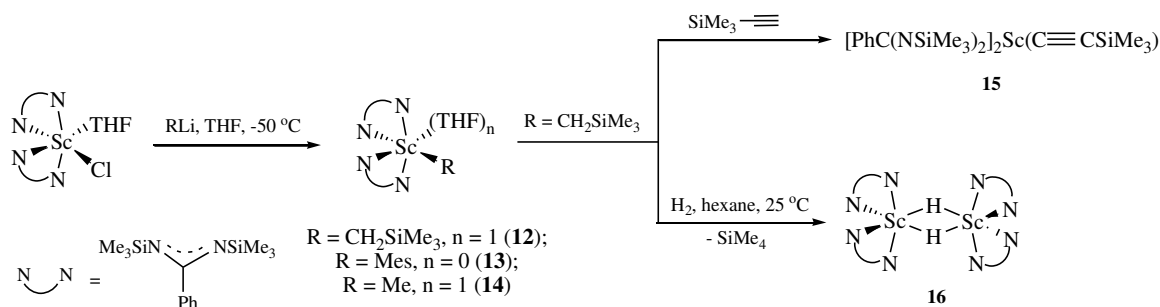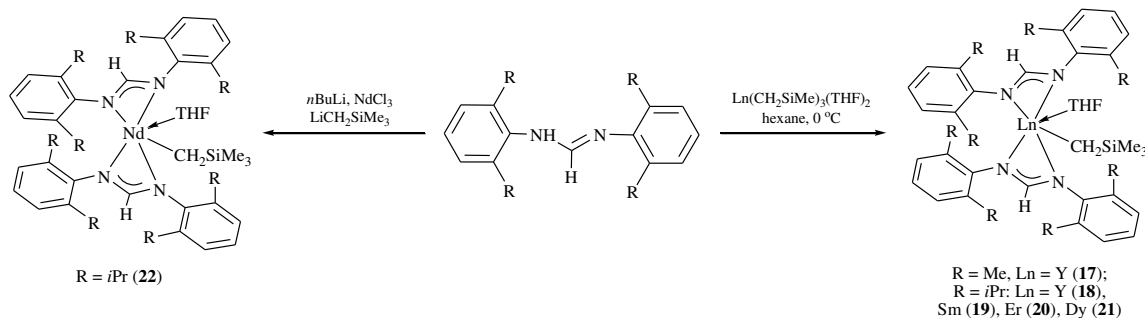
Scheme 5

gave rise to the corresponding alkyl species [HC(N-2,6-$R_2C_6H_3$)$_2$]LnCH$_2$SiMe$_3$(THF) (R = Me, Ln = Y (**17**); R = *i*Pr: Ln = Y (**18**), Sm (**19**), Er (**20**), Dy (**21**)) in good yields (Scheme 5) [39]. A similar complex of neodymium [HC(N-2,6-*i*Pr$_2C_6H_3$)$_2$]$_2$NdCH$_2$SiMe$_3$(THF) (**22**) was synthesized by the exchange reaction between NdCl$_3$ and lithium salt of formamidine [HC(N-2,6-*i*Pr$_2C_6H_3$)$_2$]Li followed by the alkylation with LiCH$_2$SiMe$_3$. According to the X-ray analyses of **18–21**, both amidinate fragments in the alkyl complexes are coordinated to the metal center through two nitrogen atoms in a κ^2-fashion.

The formamidine ligands allow for the synthesis of methyl species of the rare-earth elements with the large ionic radii, such as lanthanum and samarium. Bis(formamidinate) alkyl complexes [HC(N-2,6-*i*Pr$_2C_6H_3$)$_2$]$_2$LnMe(THF) (Ln = Sm (**23**), La (**24**)) were obtained by the reactions of chloride compounds [HC(N-2,6-*i*Pr$_2C_6H_3$)$_2$]$_2$LnCl(THF) with equimolar amounts of MeLi in toluene at room temperature (Scheme 6) [40]. Complexes **23** and **24** demonstrate extremely high stability and do not decompose in the solid state up to 250 °C.
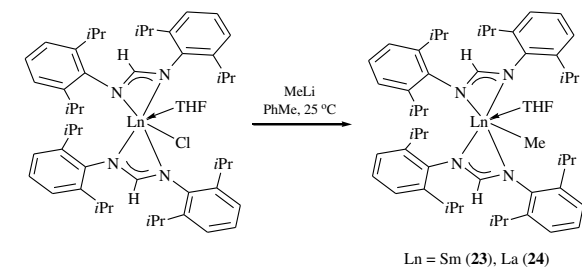
Dianionic boramidinate ligand systems, with the BH$^-$ fragment isoelectronic to amidinates, can also serve as convenient coordination environments for the synthesis and isolation of alkyl derivatives of rare-earth elements. The reaction of [2,6-*i*Pr$_2$-C$_6H_3$-NHBHNH-C$_6H_3$-*i*Pr$_2$] with equimolar amounts of tris(aminobenzyl) compounds of yttrium and

samarium Ln(*o*-CH$_2C_6H_4$NMe$_2$)$_3$ (Ln = Y, Sm) in toluene at 60 °C afforded neutral alkyl complexes [HB(N-2,6-*i*Pr$_2C_6H_3$)$_2$]Ln(*o*-CH$_2C_6H_4$NMe$_2$) (Ln = Y (**25**), Sm (**26**)) in high yields (Scheme 7) [41]. The XRD analysis showed that complex **26** is a dimer with the bridging boramidinate ligands, where each samarium atom is η^3-coordinated by the phenyl ring of *i*Pr$_2C_6H_3$-group of an adjacent fragment.
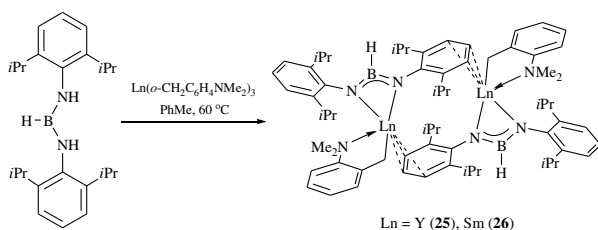
Substituted guanidinate ligands [RNC(NR')$_2$]$^-$ have found wide application in the chemistry of organic derivatives of rare-earth elements owing to the simplicity of their synthesis. The variation of substituents at the nitrogen atoms allows for modification of the electronic and steric characteristics of guanidinate ligands [42].

Bis(guanidinate) yttrium alkyl species [Me$_3$SiNC(N*i*Pr)$_2$]$_2$YR (R = *t*Bu (**27**), (Me$_3$Si)$_2$CH (**28**)) were obtained by the salt metatheses of dimeric chloride complex [((Me$_3$Si)$_2$NC(N*i*Pr)$_2$)$_2$YCl]$_2$ with alkyllithium reagents (Fig. 1) [43]. These compounds do not contain the coordinated Lewis bases, which leads to the low coordination numbers of the metal centers. More sterically bulky dicyclohexyl guanidine was successfully used to synthesize alkyl derivatives of yttrium [(Me$_3$Si)$_2$NC(NCy)$_2$]YR (R = *t*Bu (**29**), Ph (**30**), Bn (**31**)) [44], samarium, ytterbium, and erbium [(Me$_3$Si)$_2$NC(NCy)$_2$]LnCH(SiMe$_3$)$_2$ (Ln = Sm (**32**), Yb (**33**)) and [(Me$_3$Si)$_2$NC(NCy)$_2$]LnR (R = *t*Bu: Ln = Yb (**34**), Er (**35**); R = Bn: Ln = Er (**36**)) (Fig. 1) [45, 46]. It is noteworthy that the yttrium atom in complex **29** is coordinationally unsaturated, which leads to the agostic interaction between the metal center and two methyl groups of the *tert*-butyl substituent. This resuts in short Y···C contacts and significant deviations of the bond angles around the central carbon atom from tetrahedral ones [44]. According to the data of XRD analysis and ^{13}C NMR spectroscopy, this agostic interaction is present not only in the crystalline state but also in a solution of C$_6$D$_6$.

Subseqeuntly, a series of rare-earth alkyl complexes with a bulky isopropyl guanidinate ligand were synthesized [47, 48].
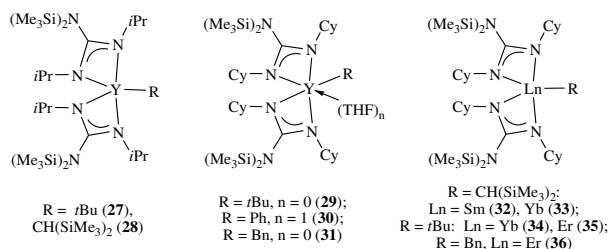
Ln = Sm (**23**), La (**24**)

Scheme 6

Ln = Y (**25**), Sm (**26**)

Scheme 7

R = *t*Bu (**27**), CH(SiMe$_3$)$_2$ (**28**)

R = *t*Bu, n = 0 (**29**);
R = Ph, n = 1 (**30**);
R = Bn, n = 0 (**31**)

R = CH(SiMe$_3$)$_2$:
Ln = Sm (**32**), Yb (**33**);
R = *t*Bu: Ln = Yb (**34**), Er (**35**);
R = Bn, Ln = Er (**36**)

Figure 1

Complexes [(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$LnCH$_2$SiMe$_3$ (Ln = Y (**37**), Lu (**38**), Sm (**39**), Nd (**40**), Gd (**41**), Yb (**42**)) were obtained by the exchange reactions between the corresponding chloride derivatives and LiCH$_2$SiMe$_3$. Treatment of alkyl complexes **37**–**42** with equimolar amounts of PhSiH$_3$ in hexane afforded dimeric hydride compounds {[(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$Ln(μ-H)}$_2$ (Ln = Y (**43**), Lu (**44**), Sm (**45**), Nd (**46**), Gd (**47**), Yb (**48**)) without coordinated Lewis bases on the metal centers (Scheme 8) [47, 48]. The X-ray analyses demonstrated that the guanidinate ligands in complexes **43**–**48** are coordinated in an asymmetric fashion in both [(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$Ln fragments.

Cui *et al*. [49] reported the synthesis of rare-earth alkyl complexes (2-tBu-C$_4$H$_2$N-4-CHN(2,6-iPr$_2$C$_6$H$_3$)YCH$_2$SiMe$_3$ (**49**) and (2-tBu-C$_4$H$_2$N-4-CHN(2,6-iPr$_2$C$_6$H$_3$)SmR (R = CH$_2$SiMe$_3$ (**50**), Me (**51**)), coordinated by a monoanionic bidentate pyrrolcarbaldiminate ligand, by the exchange reactions between the corresponding chloride derivatives and alkyllithium reagents in toluene at low temperature (Fig. 2). An attempt to synthesize the yttrium methyl complex using an analogous procedure did not lead to the desired product. According to the XRD analysis data, complex **50** is monomeric and contains two η^1-coordinated pyrrole fragments.

Zhang *et al*. used substituted imino-indoles as coordination environments for rare-earth alkyl complexes [50–52]. Binuclear alkyl species {[η^2:η^1-μ-η^1-3-(CyNCH(CH$_2$SiMe$_3$))C$_8$H$_5$N]LnCH$_2$SiMe$_3$(THF)}$_2$ (Ln = Yb (**52**), Er (**53**), Y (**54**)) were obtained upon interaction of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with equimolar amounts of 3-(CyN=CH)C$_8$H$_5$NH in toluene at room temperature (Scheme 9) [51]. The reactions in THF under similar conditions afforded binuclear complexes {[η^1-μ-η^1-3-(CyNCH(CH$_2$SiMe$_3$))C$_8$H$_5$N]LnCH$_2$SiMe$_3$(THF)}$_2$ (Ln = Yb (**55**), Er (**56**), Y(**57**), Gd (**58**)). In both cases, the reaction of 3-imino-indole with tris(alkyl) derivatives was accompanied by the insertion of CH$_2$SiMe$_3$ group into the C=N bond, resulting in a new cyclohexylamido-indole ligand system. The XRD analyses of complexes **52**–**54** showed that the indole ligand is bound to one metal center through two carbon atoms of the five-membered ring in a η^2-fashion, while the nitrogen atom of the indole fragment is bound to the other metal center in a η^1-mode. In complexes **55**–**58**, two metal atoms are connected by the nitrogen atoms of the indole ring and the amide groups. It is noteworthy that, unlike complexes **52**–**54**, the indole ligands in compounds **55**–**58** are not parallel. Moreover, six-membered rings of the indole ligands in **55**–**58** are oriented in one direction, whereas in **52**–**54** they have opposite orientations. Treatment of alkyl complexes **52**, **53**, and **54** with an excess of THF yielded compounds **55**, **56**, and **57**, respectively. The conversion of **55**–**57** to **52**–**54** can be accomplished upon boiling in toluene.

The interaction of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with an equimolar amount of a similar iminoindole bearing a *tert*-butyl group at the nitrogen atom, 3-(tBuN=CH)C$_8$H$_5$NH, in THF gave rise to binuclear complexes {[η^2:η^1-μ-η^1-3-(tBuNCH(CH$_2$SiMe$_3$))-C$_8$H$_5$N]LnCH$_2$SiMe$_3$(THF)}$_2$ (Ln = Y (**59**), Dy (**60**), and Yb (**61**)) in high yields (Scheme 10) [50]. Just as with compounds **52**–**54**, the reactions of 3-*tert*-butyl iminoindole with tris(alkyl) derivatives were accompanied by the transfer of one CH$_2$SiMe$_3$ group over the double C=N bond, resulting in a dianionic

amido-indole ligand. It is noteworthy that, unlike 3-(CyN=CH)C$_8$H$_5$NH, in the case of 3-(tBuN=CH)C$_8$H$_5$NH the binuclear complexes with η^1-μ-η^1-bound ligands were not formed.

Monomeric bis(imino-indole) alkyl complexes [η^1:η^1-2-(2,6-iPrC$_6$H$_3$N=CH)C$_8$H$_5$N]$_2$LnCH$_2$SiMe$_3$(THF) (Ln = Yb (**62**), Er (**63**), Y (**64**), Dy (**65**), Gd (**66**)) were obtained in moderate yields by the reactions of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with 2-(2,6-iPrC$_6$H$_3$N=CH)C$_8$H$_5$NH in toluene at room temperature (Scheme 11) [52]. The authors failed to synthesize an analogous

Ln = Y (**37**), Lu (**38**), Sm (**39**), Nd (**40**), Gd (**41**), Yb (**42**)

Ln = Y (**43**), Lu (**44**), Sm (**45**), Nd (**46**), Gd (**47**), Yb (**48**)

Scheme 8

Ar = 2,6-iPr$_2$C$_6$H$_3$

49

R = CH$_2$SiMe$_3$ (**50**), Me (**51**)

Figure 2

Ln = Yb (**52**), Er (**53**), Y (**54**)

Ln = Yb (**55**), Er (**56**), Y (**57**), Gd (**58**)

Scheme 9

Ln = Y (**59**), Dy (**60**), Yb (**61**)
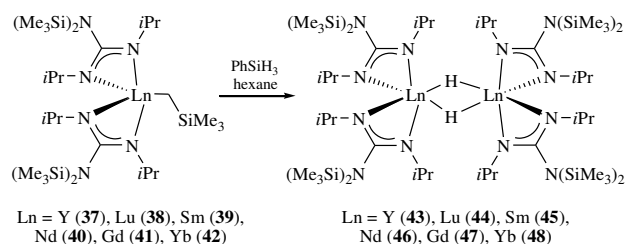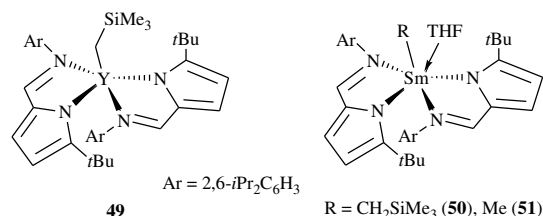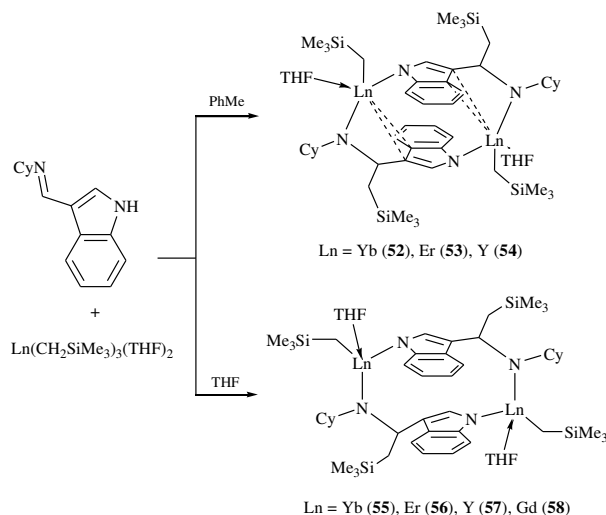
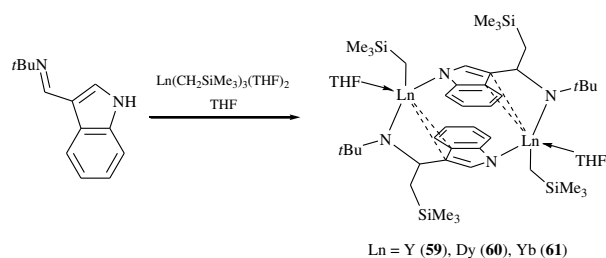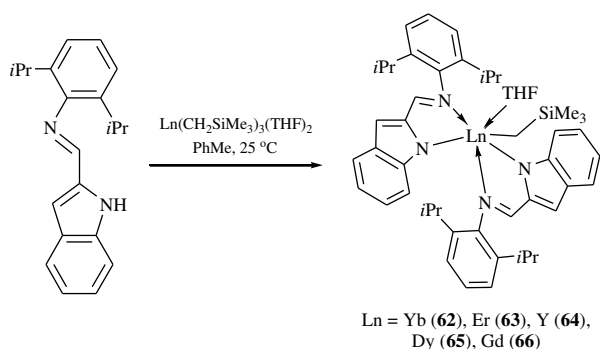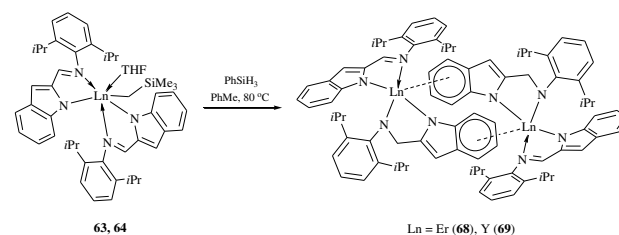**Scheme 10**

Scheme 11

samarium complex, since the interaction of the freshly prepared tris(alkyl) derivative of Sm with 2-imino-indole was accompanied by the redistribution of the ligands and the formation of $[\eta^1:\eta^1-2-(2,6-iPrC_6H_3N=CH)C_8H_5N]_3Sm$ (**67**). According to the results of XRD analysis, the coordination environments of the metal centers in complexes **62–66** are distorted octahedra.

In order to obtain hydrido derivatives of rare-earth elements stabilized by the 2-imino-indole ligand, complexes **63** and **64** were treated with $PhSiH_3$ in toluene at 80 °C. However, only binuclear compounds $\{[\mu-\eta^6:\eta^1:\eta^1-2(2,6-iPrC_6H_3NCH_2)C_8H_5N]Ln[2(2,6-iPrC_6H_3N=CH)C_8H_5N]\}_2$ (Ln = Er (**68**) and Y (**69**)) were isolated from the reaction mixtures (Scheme 12). Complexes **68** and **69** contain two μ-bridging dianionic imino-indole ligands bound to the metal centres in a μ-$\eta^6:\eta^1:\eta^1$-fashion, and two terminal monoanionic imino-indole ligands $\eta^1:\eta^1$-coordinated to the metal atoms [52].
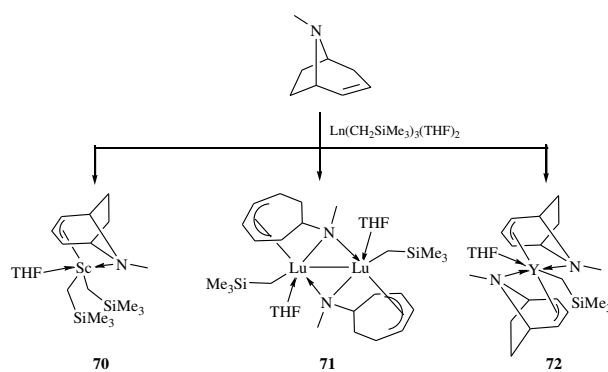
The acid-base interactions between $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Lu, and Y) and equimolar amounts of tropidine (N-methyl-1,4-cyclohepta-5,6-ene) (TropH) in hexane at room temperature afforded rare-earth alkyl complexes of variable structures, which depended on the ionic radii of the metal centers (Scheme 13) [53]. In the case of the smallest scandium ion, mono(tropidyl) bis(alkyl) complex $(Trop)Sc(CH_2SiMe_3)_2(THF)$ (**70**) was isolated in 65% yield. For lutetium, an analogous bis(alkyl) derivative appeared to be unstable and binuclear alkyl compound $[(NMCH)LuCH_2SiMe_3]_2$ (**71**) with tetradentate dianionic 6-N-methyl-1,4-cycloheptadienyl (NMCH) ligand was formed. This transformation of ligand systems is a result of the elimination of one CH_2SiMe_3 group of the initial bis(alkyl) complex $(Trop)Lu(CH_2SiMe_3)_2(THF)$, which is accompanied by the opening of the tropidinyl ring and the formation of the Lu–N bond. Finally, treatment of $Y(CH_2SiMe_3)_3(THF)_2$ with tropidine resulted in neutral alkyl complex $(Trop)_2Y(CH_2SiMe_3)(THF)$ (**72**) (Scheme 13) [53]. The structures of complexes **70–72** were confirmed by X-ray crystallography. The tropidinyl ligands in

compounds **70** and **72** are coordinated to the metal centers through the nitrogen atoms and the covalently bonded anionic allylic moieties. Each lutetium atom in dimeric complex **71** is bound to tetradentate 6-N-methyl-1,4-cycloheptadienyl ligand *via* 2σ/6π-electron-donor cyclopentadienyl moiety.
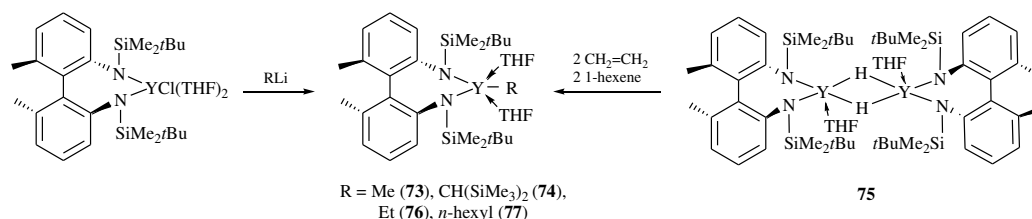
Diamido ligands, differing both in the number of donor groups and the nature and length of a bridging unit between the functional groups, are the most popular non-cyclopentadienyl ligand systems in the field of organic derivatives of rare-earth elements [54]. Sterically demanding dianionic bidentate 2,2'-bis-*tert*-butyldimethylsilylamido-6,6'-dimethyldiphenyl ligand (DADMB) was used for the synthesis of yttrium alkyl species. The coordination of DADMB to a metal atom results in the formation of a seven-membered metallocycle. Complexes (DADMB)YMe(THF)$_2$ (**73**) and (DADMB)YCH(SiMe$_3$)$_2$(THF)$_2$ (**74**) were obtained by the σ-bond metathesis of chloride compound (DADMB)YCl(THF)$_2$ with MeLi and (Me$_3$Si)$_2$CHLi, respectively (Scheme 14). Similar ethyl and *n*-hexyl derivatives of yttrium, (DADMB)YR(THF)$_2$ (R = Et (**76**), *n*-hexyl (**77**)), were synthesized by the reactions of dimeric hydride complex $\{[DADMB]Y(\mu-H)(THF)\}_2$ (**75**) with ethylene and 1-hexene in a THF solution (Scheme 14) [54]. According to the X-ray diffraction data, the molecule of complex **76** lies on a C_2 axis and the ethyl group is highly disordered between the two symmetry positions.
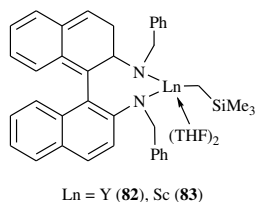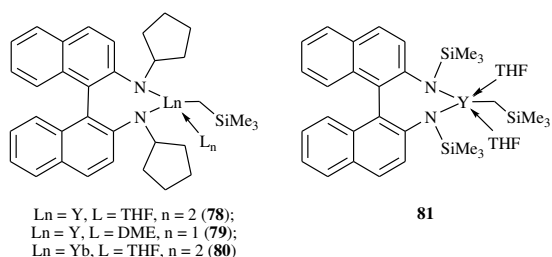

Scheme 12

Scheme 13

Scheme 14

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Ln = Y, L = THF, n = 2 (**78**);
Ln = Y, L = DME, n = 1 (**79**);
Ln = Yb, L = THF, n = 2 (**80**)

81

Ln = Y (**82**), Sc (**83**)

Figure 3

Scheme 15

n = 1: R = CH(SiMe$_3$)$_2$ (**84**), CH$_2$Ph (**85**),
n = 2 : R = CH(SiMe$_3$)$_2$ (**86**), R = CH$_2$Ph (**87**)

Ln = Y:
R^1 = R^2 = *i*Pr, R^3 = H (**88**),
R^1 = R^2 = R^3 = Me (**89**),
R^1 = R^2 = R^3 = H (**90**)

Ln = Lu:
R^1 = R^2 = *i*Pr, R^3 = H (**91**),
R1 = R^2 = R^3 = Me (**92**),
R^1 = R^2 = R^3 = H (**93**)

Scheme 16

Chiral (*R*)-binaphthylamines were used for the synthesis of neutral alkyl complexes of yttrium and ytterbium. Treatment of (*R*)-(+)-2,2'-bis(cyclopentylamino)-1,1'-binaphthyl (BinamH$_2$) with tris(alkyl) derivatives Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Y, Yb) led to the formation of alkyl complexes (Binam)LnCH$_2$SiMe$_3$(L)$_n$ (Ln = Y, L = THF, n = 2 (**78**); Ln = Y, L = DME, n = 1 (**79**); Ln = Yb, L = THF, n = 2 (**80**)) in high yields (Fig. 3) [55]. Compounds **78–80** demonstrate high stability in the crystalline state and can be stored in an inert atmosphere at 0 °C for several months without a trace of decomposition. However, in C$_6$D$_6$ at room temperature they slowly decompose with the release of SiMe$_4$. Yttrium complex (Binam)YCH$_2$SiMe$_3$(DME) (**79**) was characterized by single-crystal XRD analysis which revealed the presence of short contacts between the metal center and the carbon atoms at the *ipso*- and *ortho*-positions of the binaphtyl fragment. The synthesis of yttrium alkyl complex (Binam(SiMe$_3$)$_2$)YCH$_2$SiMe$_3$(THF)$_2$ (**81**) coordinated by the binaphthyl ligand with SiMe$_3$ groups at the nitrogen atoms instead of the cyclopentyl ones was also reported (Fig. 3) [56]. It should be emphasized that the binaphthylamido ligand with more bulky SiMe$_2$*t*Bu groups at the nitrogen atoms does not interact with Y(CH$_2$SiMe$_3$)(THF)$_2$. Complex **81** showed lower thermal stability than analogous compound **78**. The decomposition of **81** in C$_6$D$_6$ at room temperature completes in a day. The interaction of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Y, Sc) with an equimolar amount of binaphthylamine with benzyl substituents at the nitrogen atoms in THF at 25 °C gave rise to the corresponding neutral alkyl derivatives (Binam(CH$_2$Ph)$_2$)LnCH$_2$SiMe$_3$(THF)$_2$ (Ln = Y (**82**), Sc (**83**)) (Fig. 3) [57]. Complexes **82** and **83** can be stored in the solid state at –20 °C for several weeks with no evidence of decomposition.

More labile diamide ligands with ethylene and propylene linkers were used to synthesize alkyl complexes of yttrium in high yields. Alkyl and benzyl complexes (C$_6$H$_3$-2,6-*i*Pr$_2$N(CH$_2$)$_n$N-*i*Pr$_2$-2,6-C$_6$H$_3$)YR(THF)$_x$ (n = 1, R = CH$_2$Ph, x = 2 (**84**); n = 1, R = CH(SiMe$_3$)$_2$, x = 1 (**85**); n = 2, R = CH$_2$Ph, x = 2 (**86**); n = 2, R = CH(SiMe$_3$)$_2$, x = 1 (**87**)) were obtained by the salt metatheses of iodine derivatives (C$_6$H$_3$-2,6-*i*Pr$_2$N(CH$_2$)$_n$N-*i*Pr$_2$-2,6-C$_6$H$_3$)YI(THF)$_2$ (n = 1, 2) with RK (R = CH$_2$Ph, CH(SiMe$_3$)$_2$) (Scheme 15) [58, 59]. The structures of
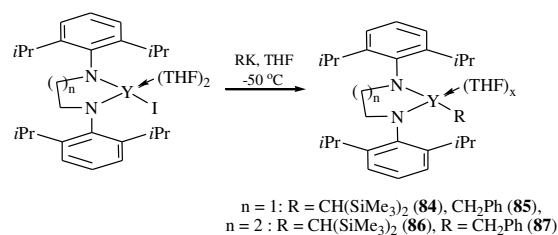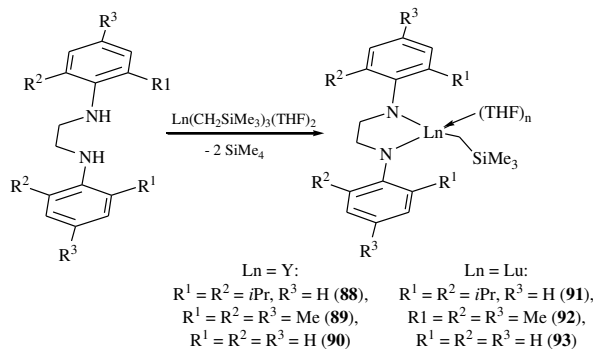
complexes **84–87** were supported by the X-ray analyses. Upon coordination to the yttrium atom, the diamide ligands form a five- or six-membered metallocycle. Compounds **84** and **85** show high stability in C$_6$D$_6$ at room temperature. In addition, they are absolutely inert towards 1-hexene and ethylene.

Related dianionic bidentate ligands ArN(CH$_2$)$_2$NAr (Ar = C$_6$H$_3$-2,6-*i*Pr$_2$, C$_6$H$_2$-2,4,6-Me$_3$, Ph) with an ethylene linker between the aryl-amide groups were used for the synthesis of alkyl complexes of yttrium **88–90** and lutetium **91–93** (Scheme 16) [59]. The reaction of alkane elimination between the diamine and tris(alkyl) derivatives Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Y, Lu) was chosen as a synthetic approach. However, only the structure of yttrium complex (C$_6$H$_3$-2,6-*i*Pr$_2$N(CH$_2$)$_2$N-*i*Pr$_2$-2,6-C$_6$H$_3$)YCH$_2$SiMe$_3$(THF)$_2$ **88**, bearing the most bulky diisopropylphenyl substituents at the nitrogen atoms, was elucidated by single-crystal XRD. The compounds of yttrium (**89**, **90**) and lutetium (**92**, **93**) with the less bulky ligands were unstable in solutions of aliphatic and aromatic solvents and were characterized only by spectroscopic methods.

The amidopyridinate ligands with a chelating monoanionic planar *N,C,N*-fragment, similar to guanidinates and amidines, proved to be convenient ligand systems for the synthesis and isolation of stable alkyl derivatives of rare-earth elements. Bulky 2,6-diisopropylphenyl-(6-(2,6-dimethylphenyl)pyridin-2-yl)amine (Ap'-H) was used for the synthesis of an yttrium alkyl complex. Compound (Ap')$_2$YCH$_2$SiMe$_3$(THF) (**94**) was obtained in 65% yield by the exchange reaction of the corresponding chloride derivative (Ap')$_2$YCl(THF) with an equimolar amount of LiCH$_2$SiMe$_3$ (Scheme 17) [60]. The structure of complex **94** was confirmed by X-ray crystallography. The coordination environment of the yttrium atom is a distorted octahedron. In order to obtain a hydride complex with the amidopyridinate ligand, compound **94** was treated with PhSiH$_3$ in toluene at room temperature. However, only complex (Ap'(Ap'-H))Y(THF) (**95**) was isolated from the reaction mixture due to the intramolecular activation of the C–H bond of one of the
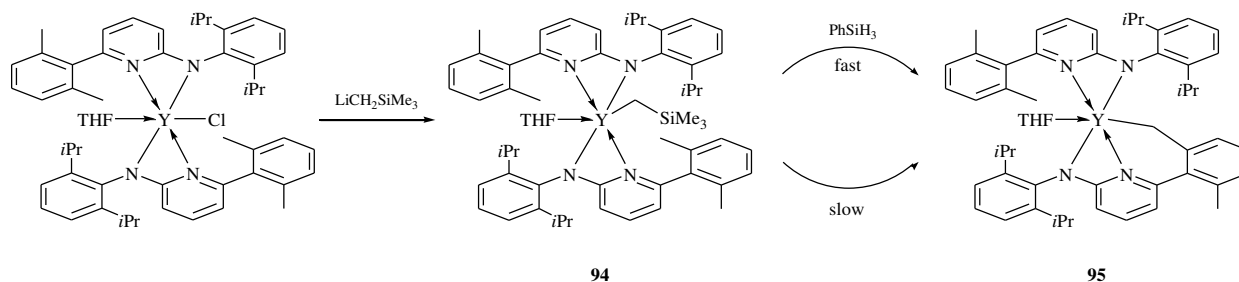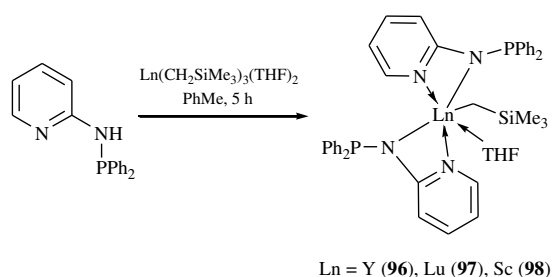
Scheme 17

methyl groups in $Me_2C_6H_3$-substituent of the ligand (Scheme 17). It is noteworthy that metallated product **95** can also be obtained by keeping complex **94** in a benzene solution at room temperature for several weeks. According to the results of XRD analysis, complex **95** is monomeric with one tridentate amidopyridinate ligand owing to the methylation of the methyl group and the formation of the new Y–C bond.

Potentially tridentate amidopyridinate ligands with a diphenylphosphine substituent, [Py-NPPh₂]⁻, were used by Cui and coworkers to synthesize neutral bis(alkyl) complexes of rare-earth elements. However, the reaction of equimolar amounts of aminopyridine [Py-NHPPh₂] with tris(alkyl) derivatives $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu, Sc) was accompanied by the elimination of two alkyl groups and afforded bis(amidopyridinate)monoalkyl complexes (Py-NPPh₂)₂LnCH₂SiMe₃(THF) (Ln = Y (**96**), Lu (**97**), Sc (**98**)) (Scheme 18) [61].

Neutral alkyl complexes (BDPPmxyl)LnCH₂SiMe₃(THF) (Ln = Sc (**99**), Lu (**100**), Y (**101**)) and (BDPPoxyl)LnCH₂SiMe₃(THF) (Ln = Sc (**102**), Lu (**103**), Y (**104**)) were obtained in good yields by the protonolysis of diamino-substituted benzenes BDPPmxyl and BDPPoxyl bearing bulky diisopropylphenyl groups with equimolar amounts of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Lu, Y) (Fig. 4) [62].
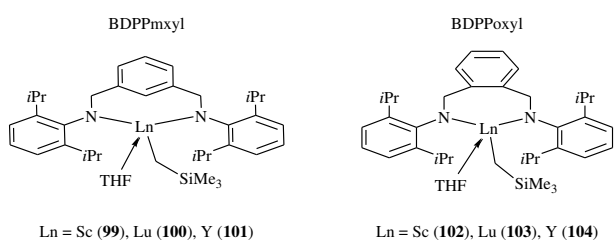
2.3. Rare-earth monoalkyl complexes with the tridentate *N*-containing ligands

A tridentate amidinate ligand with a pendant donor group in a side chain was used for the synthesis of an yttrium benzyl derivative [63]. Bis(amidinate) complex (PhC(NSiMe₃)(CH₂)₃NMe₂)₂YCH₂Ph (**105**) was obtained by the reaction of anhydrous YCl₃(THF)₃.₅ with the corresponding lithium amidinate followed by the alkylation with an equivalent of PhCH₂K (Fig. 5). The XRD analysis revealed that only one amino group of the amidinate ligands is coordinated to the yttrium atom.
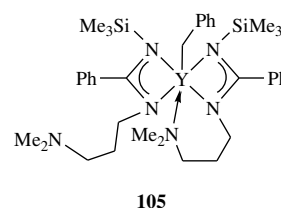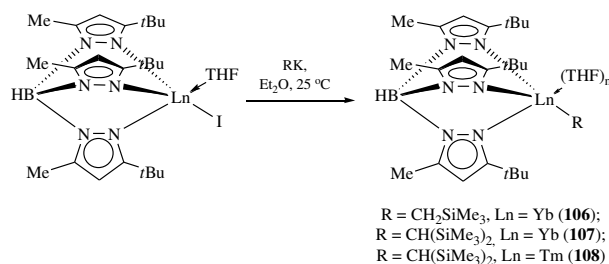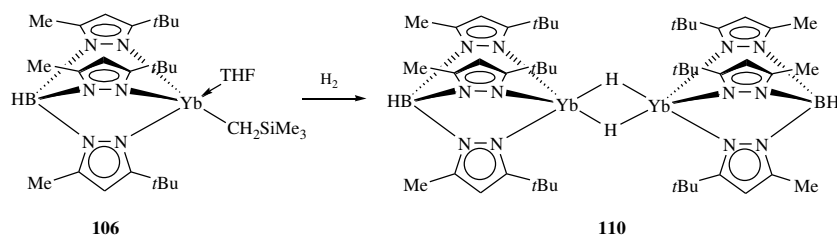

105

Figure 5

Monoanionic tridentate hydro-tris(3-*tert*-butyl-5-methylpyrazolyl)borate (Tp^{tBu,Me}) is one of the few ligands that enable the synthesis of stable alkyl derivatives of divalent ytterbium and thulium. The exchange reactions of iodine-containing compound (Tp^{tBu,Me})LnI(THF) with alkylpotassium reagents resulted in the formation of the alkyl complexes of ytterbium and thulium of a general formula (Tp^{tBu,Me})LnR(THF)$_n$ (R = CH₂SiMe₃, Ln = Yb, n = 1 (**106**); R = CH(SiMe₃)₂: Ln = Yb, n = 0 (**107**), Ln = Tm, n = 0 (**108**)) (Scheme 19) [64, 65]. The structures of complexes **107** and **108** were supproted by X-ray crystallography. Compound **107** reacts with phenylacetylene to form the corresponding acetylide derivative (Tp^{tBu,Me})YbC≡CPh (**109**) [64].

Ln = Y (**96**), Lu (**97**), Sc (**98**)

Scheme 18

Ln = Sc (**99**), Lu (**100**), Y (**101**)   Ln = Sc (**102**), Lu (**103**), Y (**104**)

Figure 4

R = CH₂SiMe₃, Ln = Yb (**106**);
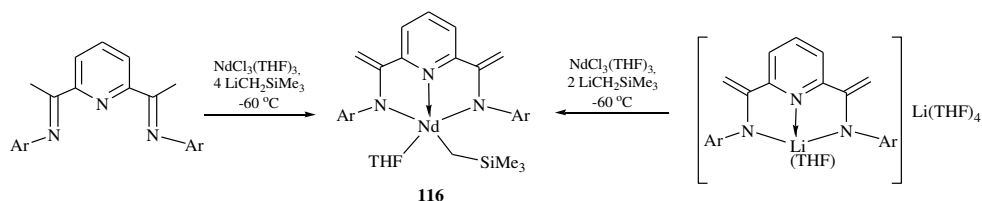R = CH(SiMe₃)₂, Ln = Yb (**107**);
R = CH(SiMe₃)₂, Ln = Tm (**108**)

Scheme 19

Scheme 20

Scheme 21

The first hydride complex of lanthanides in +2 oxidation state, $[(Tp^{t\text{-}Bu,Me})Yb(\mu\text{-}H)]_2$ (**110**), was obtained by the hydrogenation of compound **106** with H_2 (Scheme 20) [66].

The reactions of tris(alkyl) derivatives $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y, Lu) with equimolar amounts of diamino-substituted pyridines provided the corresponding rare-earth alkyl complexes (Fig. 6) [62]. Monomeric complexes (BDPPpyr)$LnCH_2SiMe_3(THF)_n$ (n = 1, Ln = Sc (**111**); n = 2, Ln = Lu (**112**); n = 2, Ln = Y (**113**)) demonstrate high stability at room temperature in hexane. The stability of the alkyl derivatives depends on the size of the ionic radius of the central metal atom. An increase in the ionic radii of the metal centers leads to a noticeable decrease in the stabilities of the alkyl complexes. Thus, compounds (BMespyr)$LnCH_2SiMe_3(THF)_n$ (n = 1, Ln = Sc (**114**); n = 2, Ln = Lu (**115**)) with smaller mesityl substituents at the nitrogen atoms were less stable under similar conditions (hexane, 20 °C). It should be noted that attempts to isolate the yttrium complex at room temperature failed.

A nonconventional approach to the synthesis of a trimethylsilylmethyl neodymium derivative with a tridentate 2,6-diiminopyridine ligand was suggested by Gambarotta *et al.* [67]. Alkyl complex $[2,6\text{-}\{[2,6\text{-}iPr_2C_6H_3]N\text{-}C=(CH_2)\}_2(C_5H_3N)]Nd(CH_2SiMe_3)(THF)$ (**116**) was obtained by the partial alkylation of $NdCl_3(THF)_3$ with alkyllithium reagent Me_3SiCH_2Li followed by the treatment with a diimine or a lithium salt of the ligand ($NdCl_3(THF)_3$/Me_3SiCH_2Li ratio 1/4 or 1/2, respectively) (Scheme 21). Dianion $[2,6\text{-}\{[2,6\text{-}iPr_2C_6H_3]N\text{-}C=(CH_2)\}_2(C_5H_3N)]^{2-}$ was formed as result of the C–H bond activation in the methyl groups at the imine carbon

atoms of $2,6\text{-}\{[2,6\text{-}iPr_2C_6H_3]N=C(CH_3)\}_2(C_5H_3N)$. The structure of complex **116** was confirmed by XRD.

Tridentate dianionic diamido-pyridinate and diamido-amino ligands have been extensively used in the chemistry of organic derivatives of rare-earth elements. Five-coordinate alkyl and aryl complexes of scandium $[(C_5H_4N)CH(Me)(CH_2NR')_2]ScR(THF)$ (R = CH_2SiMe_3, R' = $SiMe_3$ (**117**); R = CH_2SiMe_3, R' = C_6H_4Me (**118**); R = CH_2SiMe_3, R' = $C_6H_2Me_3$ (**119**); R = Ph, R' = $SiMe_3$ (**120**)), $[R'N\{(CH_2)_2NSiMe_3\}_2]ScR(THF)$ (R = CH_2SiMe_3, R' = Me (**121**); R = CH_2SiMe_3, R' = $SiMe_3$ (**122**)), $[Me_3SiN\{(CH_2)_3NSiMe_3\}_2]ScCH_2SiMe_3(THF)$ (**123**), and $[(C_5H_4N)CH_2N((CH_2)_2NSiMe_3)_2]ScCH_2SiMe_3(THF)$ (**124**) can be obtained both by the reactions of $ScR_3(THF)_2$ (R = CH_2SiMe_3, Ph) with equimolar amounts of neutral ligands and by the exchange reactions starting from $ScCl_3$ followed by the alkylation (Fig. 7) [68–70]. According to the X-ray diffraction analysis data, compounds **119** and **124** are monomeric, whereas complex $[\{(C_5H_4N)CH(Me)(CH_2NC_6H_4Me)_2\}ScCH_2SiMe_3]_2$ (**125**), deprived of the coordinated THF molecules, has a dimeric structure in the crystalline state due to the presence of two bridging amido groups.

Yttrium complexes $[(ArNCH_2CH_2)_2NMe)Y(o\text{-}CH_2C_6H_4NMe_2)]$ (Ar = $2,4,6\text{-}Me_3C_6H_2$ (**126**), $2,6\text{-}Et_2C_6H_3$ (**127**), $2,6\text{-}Cl_2C_6H_3$ (**128**)), containing σ-linked aryl ligands with additional donor groups in side chains, were obtained by arene elimination upon treatment of the corresponding tris(aryl) derivatives with amines (Scheme 22) [71]. Compound **126** features low stability in solution and decomposes at 25 °C, whereas complexes **127** and **128** are much more stable.

Chen *et al.* successfully used dianionic tridentate *N,N,N*-β-diketiminate ligands to produce a series of alkyl complexes of rare-earth elements. The reactions of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Lu, Y) with substituted β-diketimines $RNHCH_2CH_2NC(Me)CHC(Me)NH(2,6\text{-}iPr_2C_6H_3)$ (R = *t*Bu, $2,6\text{-}Me_2C_6H_3$, $2,6\text{-}iPr_2C_6H_3$) led to monoalkyl complexes $[RNHCH_2CH_2NC(Me)CHC(Me)NH(2,6\text{-}iPr_2C_6H_3)]\text{-}LnCH_2SiMe_3(THF)$ (R = *t*Bu, Ln = Y (**129**); R = $2,6\text{-}Me_2C_6H_3$, Ln = Sc (**130**); R = $2,6\text{-}Me_2C_6H_3$, Ln = Y (**131**); R = $2,6\text{-}Me_2C_6H_3$, Ln = Lu (**132**); R = $2,6\text{-}iPr_2C_6H_3$, Ln = Y (**133**))

Figure 6

R = CH$_2$SiMe$_3$, R' = SiMe$_3$ (**117**),
R = CH$_2$SiMe$_3$, R' = C$_6$H$_4$Me (**118**),
R = CH$_2$SiMe$_3$, R' = C$_6$H$_2$Me$_3$ (**119**),
R = Ph, R' = SiMe$_3$ (**120**)

R = CH$_2$SiMe$_3$, R' = Me (**121**),
R = CH$_2$SiMe$_3$, R' = SiMe$_3$ (**122**)

123　　　**124**

Figure 7

Ar = 2,4,6-Me$_3$C$_6$H$_2$ (**126**),
2,6-Et$_2$C$_6$H$_3$ (**127**),
2,6-Cl$_2$C$_6$H$_3$ (**128**)

Scheme 22

R = *t*Bu, Ln = Y (**129**),
R = 2,6-Me$_2$C$_6$H$_3$:
Ln = Sc (**130**), Y (**131**), Lu (**132**);
R = *i*Pr$_2$C$_6$H$_3$:
Ln = Y (**133**), Dy (**134**), Gd (**135**), Nd (**136**)
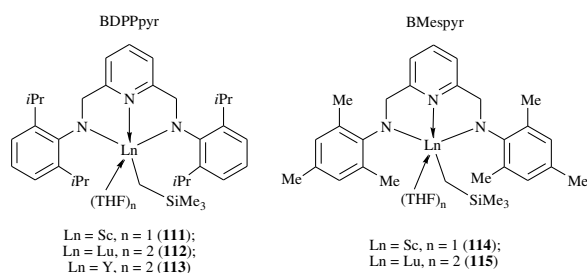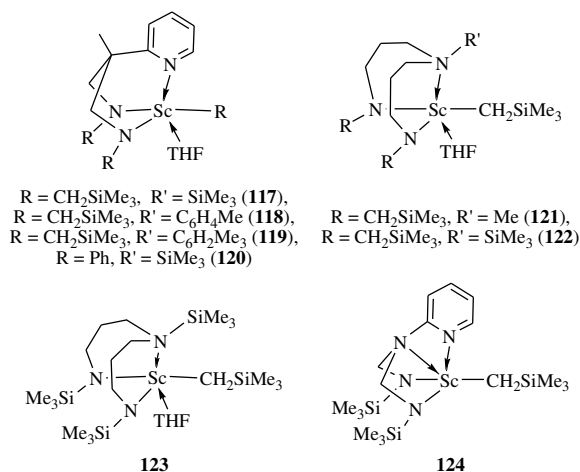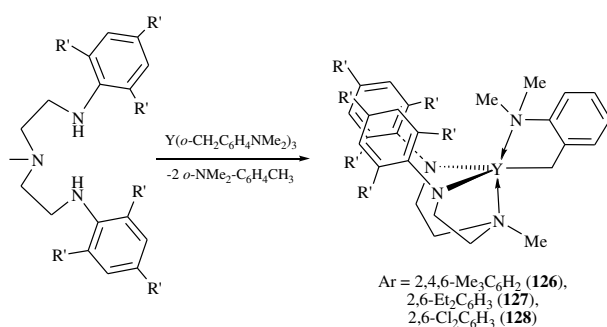
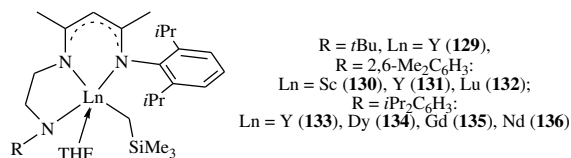**Figure 8**

(Fig. 8) [72]. Alkyl compounds of gadolinium, dysprosium and neodymium [2,6-*i*Pr$_2$C$_6$H$_3$NHCH$_2$CH$_2$NC(Me)CHC(Me)NH(2,6-*i*Pr$_2$C$_6$H$_3$)]LnCH$_2$SiMe$_3$(THF) (Ln = Dy (**134**), Gd (**135**), Nd (**136**)) with the most bulky diisopropylphenyl substituents in side chains were obtained by the protonolysis of the freshly prepared tris(alkyl) derivatives with equimolar amounts of the corresponding β-diketimines (Fig. 8). The XRD analyses demonstrated that the coordination environments in complexes **129**, **131**, and **136** are distorted square pyramids with alkyl groups at the apical positions.

2.4. Rare-earth monoalkyl complexes with the polydentate *N*-containing ligands

Alkyl complexes with tetradentate dianionic ligands are represented by *ansa*-linked bis(amidinate) [(CH$_2$)$_3${N(CPh)NSiMe$_3$}$_2$]YCH(SiMe$_3$)$_2$(THF) (**137**) [73] and guanidinate [(CH$_2$)$_3${N(CN(*i*Pr)(SiMe$_3$))N*i*Pr}$_2$]-SmCH$_2$Ph(DME) (**138**) [74]. These compounds were synthesized by the exchange reactions of the corresponding

chloride derivatives with alkyllithium or alkylpotassium reagents (Fig. 9).

The syntheses of yttrium and lutetium alkyl complexes with tetradentate bis(amidinate) ligands containing *ortho*-phenylene linkers were also reported [75]. Complexes [C$_6$H$_4$-1,2-{NC(*t*Bu)N(2,6-R$_2$C$_6$H$_3$)}$_2$]Ln(CH$_2$SiMe$_3$)(THF)$_n$ (R = Me, Ln = Y, n = 1 (**139**); R = Me, Ln = Lu, n = 1 (**140**); R = *i*Pr, Ln= Y, n = 2 (**141**)) were obtained by the reactions of equimolar amounts of tris(alkyl) derivatives Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and the corresponding bis(amidine) (Fig. 10). Compounds **139**–**141** are quite stable in the solid state and can be stored in an inert atmosphere at 0 °C for several months without evidence of decomposition. The structures of complexes **139** and **140** were confirmed by single-crystal X-ray analyses.

Tetradentate dianionic aminotropominate ligands were successfully used for the synthesis and isolation of alkyl derivatives of rare-earth elements **142**, **143**, and **144** (Fig. 11) [76].
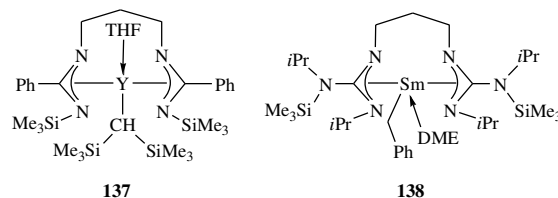

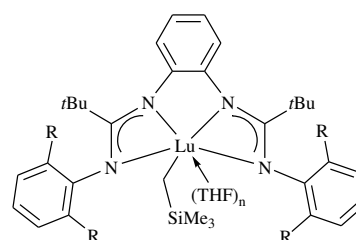**137**　　　**138**
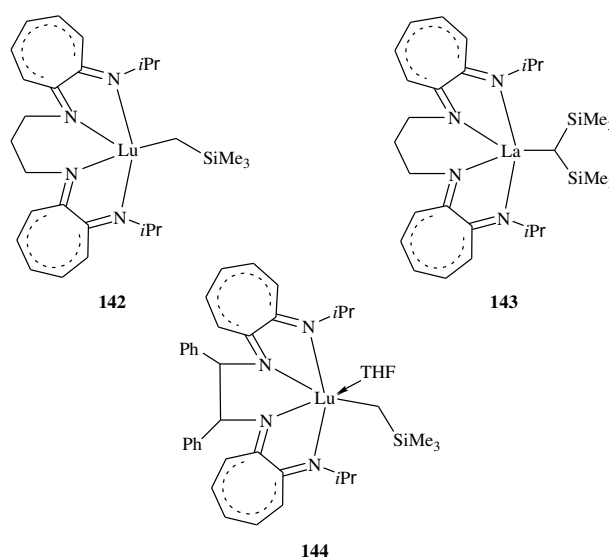
Figure 9

R = Me, n = 1: Ln = Y (**139**), Lu (**140**);
R = *i*Pr, n = 2, Ln = Y (**141**)

Figure 10

142　　　**143**

144

Figure 11

Ln = Y, R = CH(SiMe$_3$)$_2$ (**145**);
Ln = Lu, R = CH(SiMe$_3$)$_2$ (**146**);
Ln = Sc: R = Me (**147**), CH$_2$SiMe$_3$ (**148**), CH(SiMe$_3$)$_2$ (**149**)
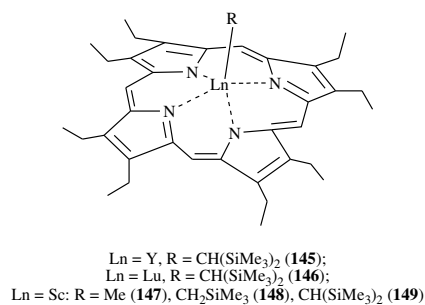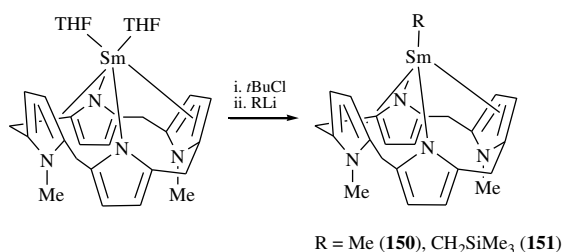
Figure 12

R = Me (**150**), CH$_2$SiMe$_3$ (**151**)

Scheme 23

Rare-earth complexes with macrocyclic ligands are of particular interest owing to their luminescence and magnetic properties [77]. However, there are only a few examples of the application of nitrogen-containing macrocyclic ligand systems as coordination environments for alkyl derivatives of lanthanides. A doubly deprotonated octaethylporphyrinic (OEP) macrocycle was used to synthesize alkyl complexes of yttrium and lutetium (OEP)LnCH(SiMe$_3$)$_2$ (Ln = Y (**145**), Lu (**146**)) [78] as well as scandium (OEP)ScR (R = Me (**147**), CH(SiMe$_3$)$_2$ (**148**), CH$_2$SiMe$_3$) (**149**) (Fig. 12) [79]. Compounds **145** and **146** resulted in high yields from the alkane elimination during the reactions between Ln[CH(SiMe$_3$)$_2$]$_3$ (Ln = Y, Lu) and octaethylporphyrin (OEPH$_2$). Complexes **145** and **146** can also be obtained by the treatment of the corresponding phenolate complexes (OEP)Ln(O-2,6-*t*BuC$_6$H$_3$) (Ln = Y, Lu) with LiCH(SiMe$_3$)$_2$. Compounds **145** and **146** feature high stability and do not decompose even upon heating in toluene at 60 °C for 6 h. The structure of lutetium complex **146** was elucidated by XRD. The coordination environment of the lutetium atom appeared to be a distorted square pyramid due to the coordination of the octaethylporphyrinic ligand and the alkyl group. Scandium derivatives **147**–**149** were synthesized by the exchange reactions of chloride complexes (OEP)ScCl with alkyllithium reagents. According to the X-ray diffraction data, compounds **147** and **148** have structures similar to that of the lutetium complex.

Treatment of complexes **145** and **146** with HO-2,6-*t*Bu-C$_6$H$_3$, *t*BuC≡CH, and H$_2$O leads to monomeric phenolate derivatives (OEP)Ln(O-2,6-*t*Bu-C$_6$H$_3$), dimeric acetylides [(OEP)Ln(μ-C≡C*t*Bu)]$_2$, and dimeric hydroxo compounds [(OEP)Ln(μ-OH)]$_2$, respectively. It is noteworthy that alkylderivatives **145** and **146** do not react with molecular hydrogen even at the high pressure (25 atm, 25 °C).

Scandium complexes **147**–**149** readily react with the C≡O bond of carbon monoxide and the C≡N bond of xylyl isocyanate, but in all cases inseparable mixtures of products

were derived. The reactions of methyl derivative (OEP)ScMe (**147**) with CO$_2$ and *trans-N,N*-dimethylated porphyrinogen (PORF) afforded stable monomeric alkyl complexes of trivalent samarium that lack the coordinated solvent molecules or alkali metal halides (compounds (PORF)SmR with R = Me (**150**) or CH$_2$SiMe$_3$ (**151**)) (Scheme 23) [80]. Alkyl derivatives **150** and **151** were synthesized by the oxidation of divalent samarium complex (PORF)Sm(THF)$_2$ with *tert*-butyl chloride followed by the alkylation with the corresponding RLi salt. The structures of complexes **150** and **151** were supported by X-ray crystallography. Unlike the methyl derivatives of samarium metallocene complexes, compound **150** appeared to be quite inert: it does not activate the C–H bond of benzene, alkenes or diethyl ether. The reactions of **150** with carbon dioxide and acetone resulted in the acetate and *tert*-butoxide complexes, respectively [79].

3.1. Rare-earth bis(alkyl) complexes with the monodentate *N*-containing ligands

N-Substituted anilines have proved to be excellent ligands for the synthesis of bis(alkyl) derivatives of rare-earth elements. Complexes [2,6-*i*Pr$_2$C$_6$H$_3$N(SiMe$_3$)]Ln(CH$_2$SiMe$_3$)$_2$(THF) (Ln = Sc (**152**), Y (**153**), Ho (**154**), Lu (**155**)) stabilized by *N*-trimethylsilyl-2,6-diisopropylanilide were prepared by the reactions of equimolar amounts of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with 2,6-*i*Pr$_2$C$_6$H$_3$NH(SiMe$_3$) (Fig. 13) [81]. In the case of gadolinium, this reaction was accompanied by the intramolecular activation of the methyl C–H bond of SiMe$_3$ group in the anilide ligand followed by the redistribution of the ligands, which resulted in bimetallic complex Gd$_2$(μ-CH$_2$SiMe$_2$NC$_6$H$_3$*i*Pr$_2$-2,6)$_3$(THF)$_3$ (**156**). Interestingly, bis(alkyl) complexes **152**–**155** do not interact with the second equivalent of 2,6-*i*Pr$_2$C$_6$H$_3$NH(SiMe$_3$).

The reaction of (*t*Bu$_2$bpy)Lu(CH$_2$SiMe$_3$)$_3$ (*t*Bu$_2$bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) with H$_2$NC$_6$H$_3$*i*Pr$_2$-2,6 in toluene led to a tris(amide) lutetium complex. The use of a more bulky aniline, namely, H$_2$NC$_6$H$_2$*t*Bu$_3$-2,4,6 ensured the high-yield synthesis of mono(amido) bis(alkyl) complex (*t*Bu$_2$bpy)Lu(NHC$_6$H$_2$*t*Bu$_3$-2,4,6)(CH$_2$SiMe$_3$)$_2$ (**157**) (Scheme 24) [82]. Treatment of compound **157** with Ph$_3$P=O promoted the replacement of *t*Bu$_2$bpy in the metal coordination sphere, resulting in the corresponding adduct (Ph$_3$P=O)$_2$Lu(NHC$_6$H$_2$*t*Bu$_3$-2,4,6)(CH$_2$SiMe$_3$)$_2$ (**158**) [82].

Scandium, yttrium, and lutetium bis(alkyl) complexes of a general formula [Im^{Ar}N]Ln(CH$_2$R)$_2$(THF)$_n$ (R = SiMe$_3$, Ln = Sc, n = 1 (**159**); R = SiMe$_3$, Ln = Y, n = 2 (**160**); R = SiMe$_3$, Ln = Lu, n = 2 (**161**); R = Ph, Ln = Lu, n = 2 (**163**)) (Im^{Ar}N = 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-imine ligand) were obtained by the reactions of the corresponding dichloride compounds [(Im^{Ar}N)LnCl$_2$(THF)$_3$] with two equivalents of LiCH$_2$SiMe$_3$ or KCH$_2$Ph (Scheme 25) [83]. Note that gadolinium derivative [(Im^{Ar}N)Gd(CH$_2$SiMe$_3$)$_2$(THF)$_2$] (**162**) was prepared from ate-complex [(Im^{Ar}N)GdCl$_2$(THF)$_2$]·[LiCl(THF)$_2$] [83]. Treatment of complexes **159**–**161** with one equivalent of zwitterionic compound [*nido*-Me$_2$NHCH$_2$CH$_2$)C$_2$B$_9$H$_{11}$] in THF afforded dicarbolide complexes with additional donor groups [(Im^{Ar}N)M{σ:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$}(THF)] (Ln =

Sc (**164**), Y (**165**), Lu (**166**)) in high yields (Scheme 26) [84]. Yttrium dicarbolide complexes containing two amine ([(Im^{Ar}N)Y{σ:σ:η^5-(Me$_2$NCH$_2$)$_2$C$_2$B$_9$H$_9$}(THF)] (**167**)) or amine and ester groups ([(Im^{Ar}N)Y{σ:σ:η^5-(Me$_2$NCH$_2$CH$_2$)(MeOCH$_2$CH$_2$)C$_2$B$_9$H$_9$}] (**168**)) in the ligand frameworks were synthesized by similar reactions (Scheme 26) [84].

Ln = Sc (**152**), Y (**153**), Ho (**154**), Lu (**155**)

156

Figure 13

Solv = tBu$_2$bpy, n = 1 (**157**);
Solv = Ph$_3$PO, n = 2 (**158**)

Scheme 24

n = 1, Ln = Sc (**159**);
n = 2: Ln =Y (**160**), Lu (**161**), Gd (**162**)

163

Scheme 25

159-161

168

167

Ln = Sc (**164**), Y (**165**), Lu (**166**)
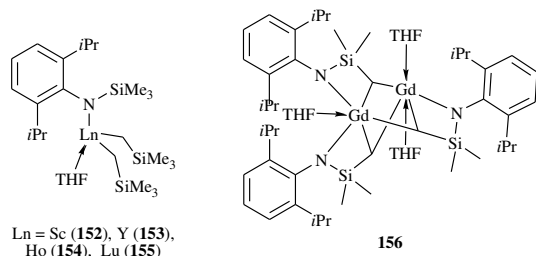
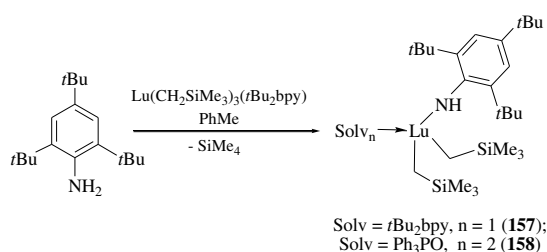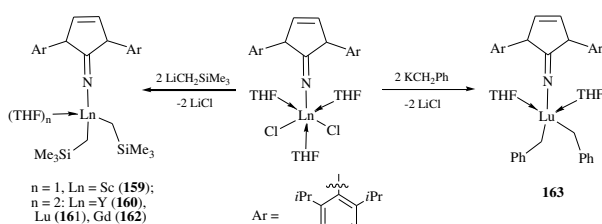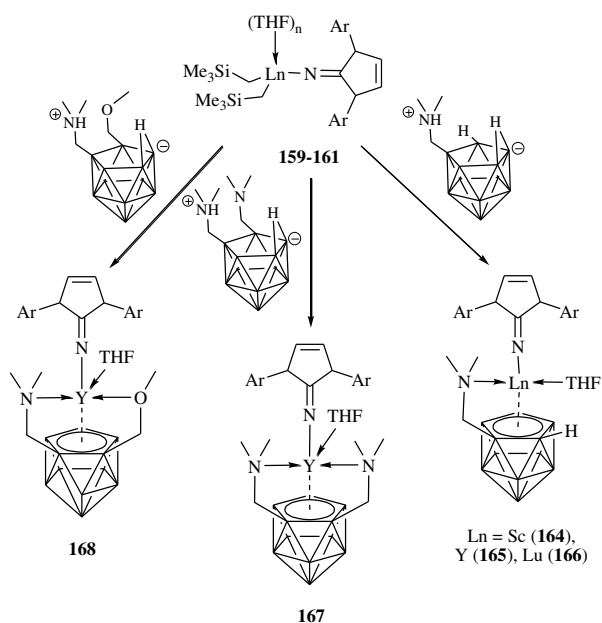**Scheme 26**

3.2. Rare-earth bis(alkyl) complexes with the bidentate *N*-containing ligands

Monoanionic chelate amidinate, guanidinate and diiminophosphinate ligands have been widely used in the chemistry of organic derivatives of lanthanides for the synthesis of mono- and bis(alkyl) complexes.
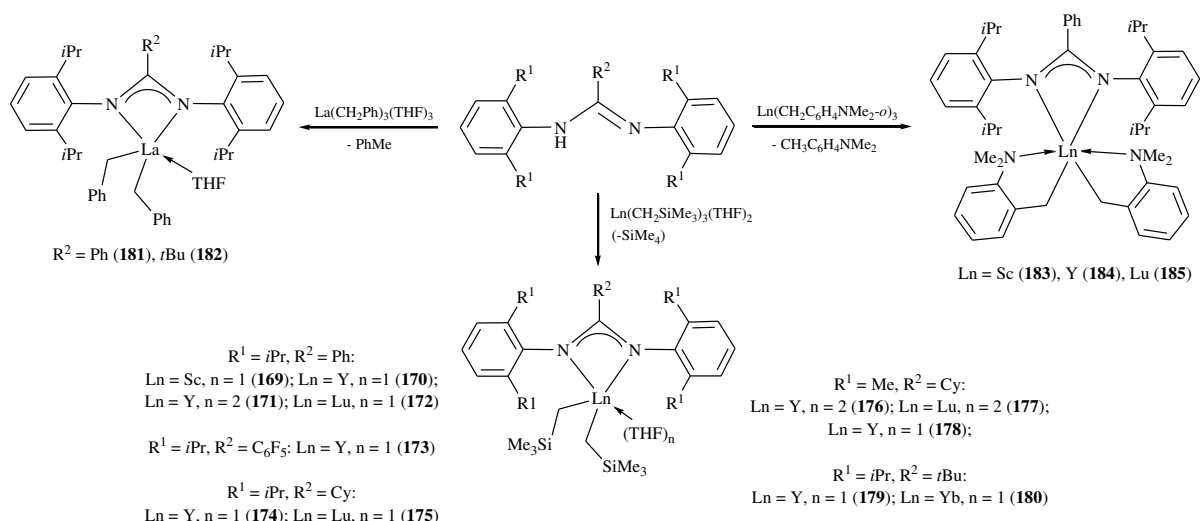
Stable rare-earth bis(alkyl) amidinate complexes [PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_n$ (Ln = Sc, n = 1 (**169**) [85]; Ln = Y: n= 1 (**170**), 2 (**171**) [86, 87]; Ln = Lu, n= 1 (**172**) [86]), [(C$_6$F$_5$)C(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (**173**) [88], [CyC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF) (Ln = Y (**174**), Lu (**175**)) [89], [CyC(NC$_6$H$_3$Me$_2$-2,6)$_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (Ln = Y (**176**), Lu (**177**)) [89], [PhC(NC$_6$H$_3$Me$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (**178**) [89], [tBuC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF) (Ln = Y (**179**) [90], Yb (**180**) [91]) resulted from the alkane elimination during the reaction of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) with the corresponding amidines (Scheme 27). Dibenzyl complexes of lanthanum [RC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]La(CH$_2$Ph)$_2$(THF) (R = Ph (**181**) [92, 93], tBu (**182**) [93]) with bulky benzamidines were also isolated in high yields (Scheme 27).

According to the XRD analysis data, in complex **182** two benzyl groups are bound in a η^2-fashion, whereas in complex **181** there are one η^3- and one η^2-benzyl groups [91]. The alkane elimination appeared to be a convenient synthetic method for the preparation of mono(amidinate) bis(aminobenzyl) rare-earth complexes [PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$C$_6$H$_4$NMe$_2$-o)$_2$ (Ln = Sc (**183**) [94], Y (**184**) [95], Lu (**185**) [94]) that do not have coordinated solvent molecules (Scheme 27). Complexes **183**–**185** and [Me$_2$NC$_6$H$_4$CH$_2$C(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$C$_6$H$_4$NMe$_2$-o)$_2$ (Ln = Sc (**186**), Lu (**187**)) can also be obtained by the metathesis between anhydrous LnCl$_3$ and lithium amidine derivative [RC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Li (R = Ph, CH$_2$C$_6$H$_4$NMe$_2$-o) followed by the alkylation with LiCH$_2$C$_6$H$_4$NMe$_2$-o [96].

Related tris(alkyl) derivatives of lanthanides with the large ionic radii Ln(CH$_2$SiMe$_3$)$_3$(THF)$_n$ (Gd, Nd, La) were synthesized without isolation by the reactions of LnX$_3$(THF)$_n$ (Ln = La, X = Br, n = 4; M = Gd, Nd, X = Cl, n = 3) with three equivalents of Me$_3$SiCH$_2$Li in THF. The subsequent addition of one equivalent of the amidine gave rise to the corresponding bis(alkyl) complexes PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (Ln = La (**188**), Nd (**189**), Gd (**190**)) in good yields (Fig. 14) [86]. For neodymium, in the case of [CyC(NC$_6$H$_3$iPr$_2$-2,6)$_2$] ligand, ate-complex [CyC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Nd(CH$_2$SiMe$_3$)$_2$(μ-Cl)Li(THF)$_3$ (**192**) was isolated in 48% yield, while the use of a less bulky amidinate ligand, namely, [CyC(NC$_6$H$_3$Me$_2$-2,6)$_2$] resulted in neutral bis(alkyl) complex [CyC(NC$_6$H$_3$Me$_2$-2,6)$_2$]Nd(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (**191**) in 52% yield (Fig. 14) [89].

Complex [Me$_3$SiCH$_2$C(NCy)$_2$]Lu(CH$_2$SiMe$_3$)$_2$(4,4'-tBu$_2$-2,2'-bipy) (**193**) (Scheme 28) [82] was synthesized by the addition of carbodiimide CyN=C=NCy to the Lu–C bond of tris(alkyl) derivative Lu(CH$_2$SiMe$_3$)$_3$(4,4'-tBu$_2$-2,2'-bpy).

Treatment of neutral mono(amidinate) bis(alkyl) complexes [PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF)$_n$ (**170**, **171**) with the Brönsted acid [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] in THF-d_8 and [PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_n$ (Ln = Sc (**169**), Y (**170** and **171**), La (**188**), Nd (**189**), Gd (**190**), Lu (**172**)) with
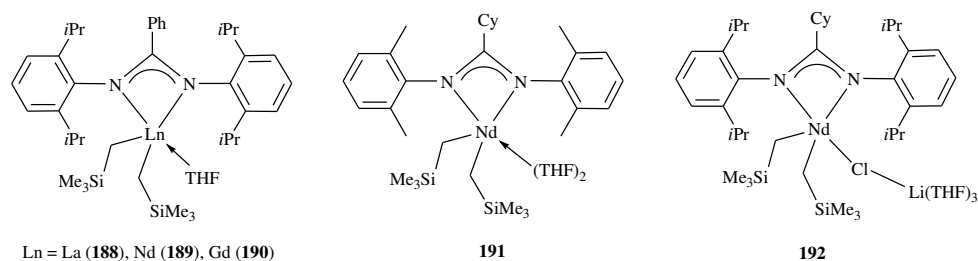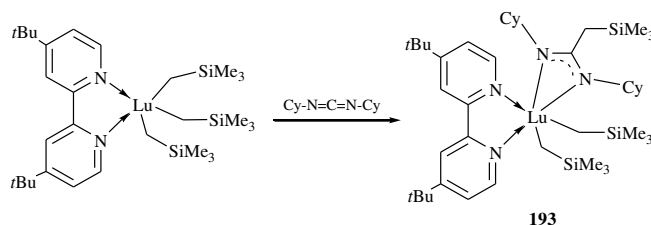
R^2 = Ph (**181**), *t*Bu (**182**)

R^1 = *i*Pr, R^2 = Ph:
Ln = Sc, n = 1 (**169**); Ln = Y, n =1 (**170**);
Ln = Y, n = 2 (**171**); Ln = Lu, n = 1 (**172**)

R^1 = *i*Pr, R^2 = C_6F_5: Ln = Y, n = 1 (**173**)

R^1 = *i*Pr, R^2 = Cy:
Ln = Y, n = 1 (**174**); Ln = Lu, n = 1 (**175**)

R^1 = Me, R^2 = Cy:
Ln = Y, n = 2 (**176**); Ln = Lu, n = 2 (**177**);
Ln = Y, n = 1 (**178**);

R^1 = *i*Pr, R^2 = *t*Bu:
Ln = Y, n = 1 (**179**); Ln = Yb, n = 1 (**180**)

Ln = Sc (**183**), Y (**184**), Lu (**185**)

Scheme 27

Ln = La (**188**), Nd (**189**), Gd (**190**)   **191**   **192**

Figure 14

193

Scheme 28

[HNMe$_2$Ph][BPh$_4$] in THF afforded cationic alkyl derivatives [{PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$}Y(CH$_2$SiMe$_3$)(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**194**) [87] and [{PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$}Ln(CH$_2$SiMe$_3$)(THF)$_n$]$^+$ [BPh$_4$]$^-$ (Ln = Sc, n = 2 (**195**); Ln = Y, n = 3 (**196**); Ln = La, n = 4 (**197**); Ln = Nd, n = 4 (**198**); Ln = Gd, n = 3 (**199**); Ln = Lu, n = 3 (**200**)) [88].

These reactions were accompanied by the formation of SiMe$_4$ and PhNMe$_2$. XRD studies showed that the remaining alkyl groups occupy axial positions [86]. Cationic lanthanum complex [{PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$}La(CH$_2$Ph)(THF)$_3$]$^+$[BPh$_4$]$^-$ (**201**) was synthesized by the reaction of the corresponding dibenzyl derivative **181** with [HNMe$_2$Ph][BPh$_4$] in THF [93].

Heterotrinuclear complexes [PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$]Ln[(μ^2-Me)$_2$AlMe$_2$]$_2$ (Ln = Sc (**202**) [94], Y (**203**) [95], Lu (**204**) [94]) were synthesized by the reactions of [PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$]Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ **183–185** with AlMe$_3$ (molar ratios: 1:5 for Y; 1:3 for Sc and Lu) in toluene at room temperature (Scheme 29). In the case of complexes [PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$]Ln(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (Ln = Sc (**183**), Lu (**185**)), treatment with two equivalents of AlMe$_3$ furnished

homometallic trinuclear methylidene complexes {[PhC(NC$_6$H$_3$*i*Pr-2,6)$_2$]Ln(μ^2-CH$_3$)$_3$(μ^3-CH$_3$)(μ^3-CH$_2$) (Ln = Sc (**205**), Lu (**206**)) (Scheme 29) in 76% and 72% yields, respectively [94].

Bis(alkyl) yttrium complexes [(Me$_3$Si)$_2$NC(NR)$_2$]-Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (R = *i*Pr (**207**) [97], Cy (**208**) [98]) and [(Me$_3$Si)$_2$NC(N*i*Pr)$_2$]Y*t*Bu$_2$(THF)$_2$ (**209**) stabilized by guanidinate ligands were obtained by the alkylation of the corresponding dichloride compounds with RLi (R = CH$_2$SiMe$_3$, *t*Bu), while complex [Me$_2$NC(NC$_6$H$_3$*i*Pr-2,6)$_2$]Y(CH$_2$SiMe$_3$)$_2$(THF) (**210**) [99] was synthesized by the alkane elimination (Fig. 15).

A series of rare-earth bis(alkyl) complexes with iminophosphonamide ligands [Ph$_2$PNAr^{1}Ar^2]-Ln(CH$_2$SiMe$_3$)$_2$(THF) (Ln = Sc (**211–213**), Y (**214–216**), Er (**217**), Lu (**218–228**)), which possess different steric and electronic properties, were synthesized by the deprotonation of iminophosphonamines with equimolar amounts of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Scheme 30) [100–102]. According to the results of X-ray crystallography, bidentate ligands
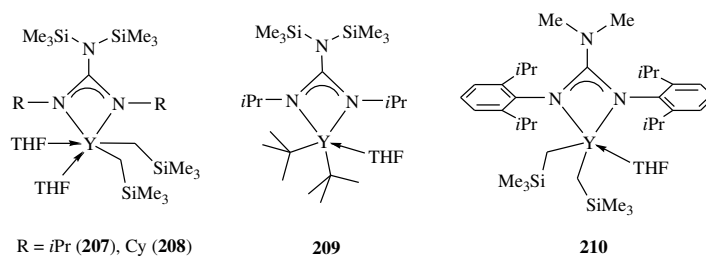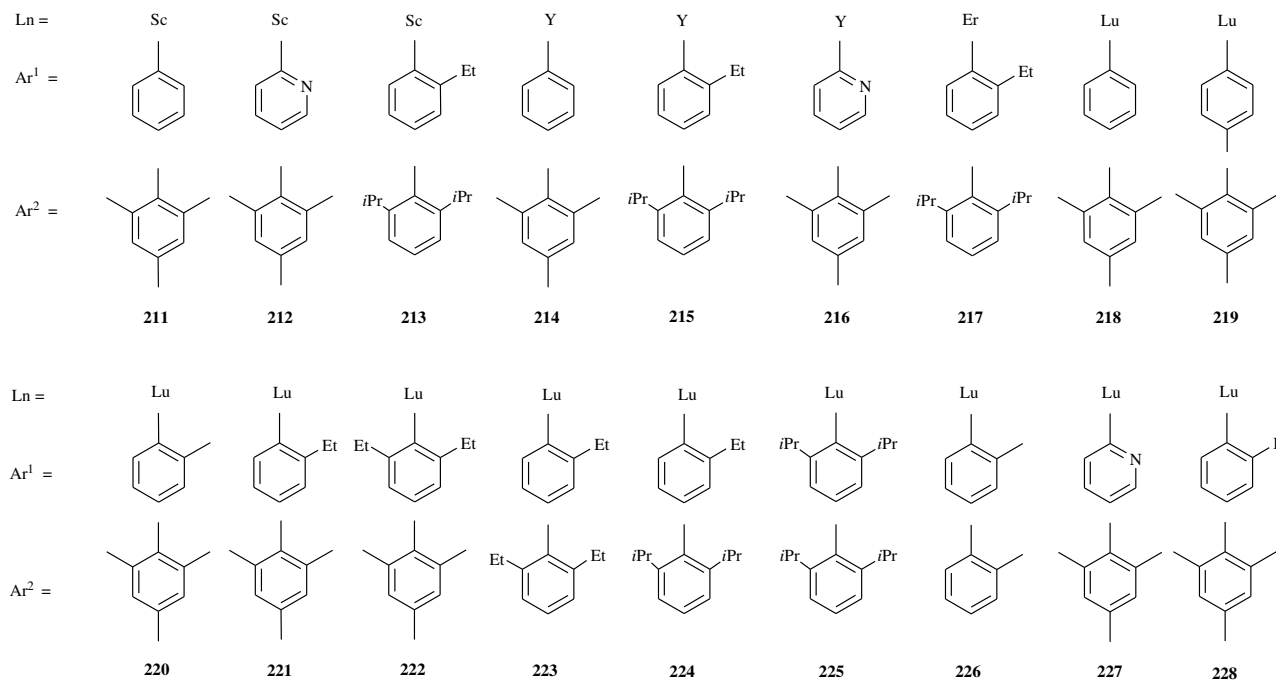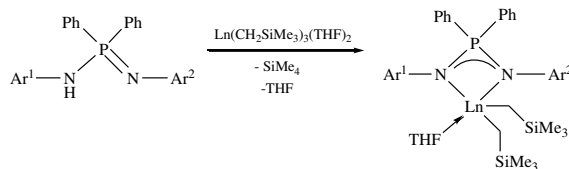
Scheme 29

R = *i*Pr (**207**), Cy (**208**)   **209**   **210**
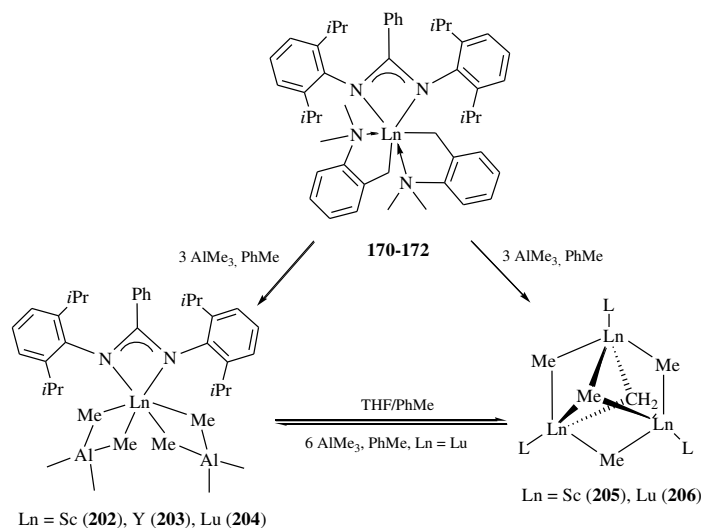
Figure 15

Scheme 30

$[Ph_2PNAr^1Ar^2]^-$ are coordinated to the Ln^{3+} metal center in a η^2-*N,N*-fashion in the meridional configuration, leading to the separation of two alkyl groups.
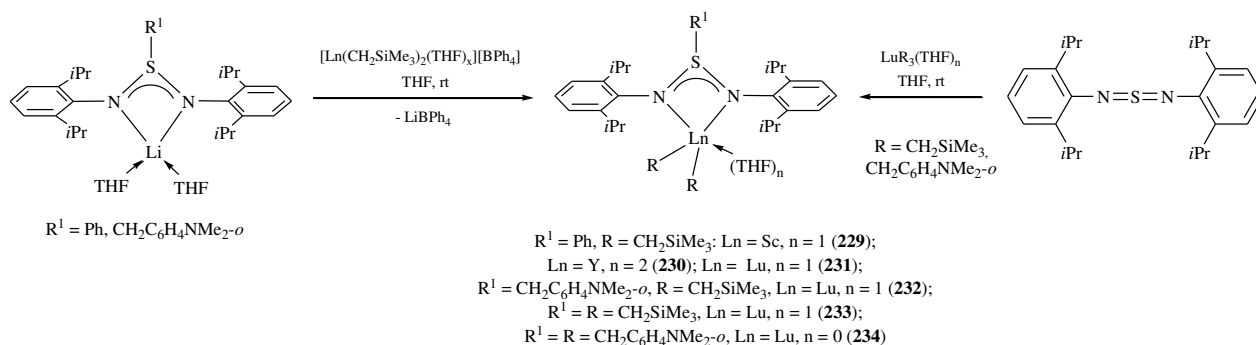
The pyridyl-iminophosphonamide can serve as an *N,N,N*-tridentate ligand (**216** and **217**) [101]. In contrast, in the case of Sc (**212**), which has the smallest ionic radius, this pyridyl-iminophosphonamide ligand is bound to the metal center in a η^2-*N,N*-mode [100].

Bis(alkyl) complexes of rare-earth elements containing β-diiminesulfonate ligands $[R^1S(NC_6H_3iPr-2,6)_2]LnR_2(THF)_n$ (R = CH_2SiMe_3, R^1 = Ph: Ln = Sc, n = 1 (**229**); Ln = Y, n = 2 (**230**); Ln = Lu, n = 1 (**231**); R = CH_2SiMe_3, R^1 = $CH_2C_6H_4NMe_2$-*o*, Ln = Lu, n = 1 (**232**)) were obtained by the reactions of cationic bis(alkyl) derivatives $[Ln(CH_2SiMe_3)_2(THF)_x]^+[BPh_4]^-$ (Ln = Sc, Y, Lu) with one equivalent of lithium salts synthesized by treating 2,6-$iPr_2C_6H_3N=S=NC_6H_3iPr_2$-2,6 with alkyllithium reagents R^1Li (R^1 = Ph, $CH_2C_6H_4NMe_2$-*o*) (Scheme 31) [102]. The reaction of alkane elimination can also be used successfully for the preparation of bis(alkyl) complexes $[R^1S(NC_6H_3iPr_2$-2,6)_2]LuR_2(THF)_n$ (R = R^1 = CH_2SiMe_3, n = 1 (**233**); R = R^1 = $CH_2C_6H_4NMe_2$-*o*, n = 0 (**234**)) (Scheme 31) [102].

Bulky amidopyridine ligands are suitable coordination environments for stabilization of rare-earth bis(alkyl) complexes. The use of these ligands allowed for the synthesis of a large number of stable bis(alkyl) derivatives of Sc, Y, Er, Yb, and Lu (compounds **235–249**) (Fig. 16) [103–108]. Most of these complexes were obtained by the alkane elimination upon interaction of $Ln(CH_2SiMe_3)_3(THF)_2$ with the corresponding aminopyridine [103]. However, the alkylation of the parent dichloride complexes of yttrium and lutetium with two equivalents of $LiCH_2SiMe_3$ also resulted in bis(alkyl) derivatives **236** and **239** in good yields [104]. XRD analysis revealed that the amidopyridine ligands are coordinated to the metal center through the amide and pyridyl nitrogen atoms. Unlike amidinate complexes, no averaging of the Ln–N bond lengths was observed for compounds **235–249** containing similar *N,C,N*-frameworks.

It was found that the length of a linker between the amide and pyridine fragments of amidopyridine ligands is crucial for stability of bis(alkyl) complexes. Bis(alkyl) derivatives stabilized by bulky *N,C,N*-amidopyridine ligands with directly attached amide and pyridinate groups feature high thermal stability. For example, yttrium complex **236** decomposes in C_6D_6 at room temperature during a week only by 10%, while analogous lutetium complex **239** does not undergo decomposition even in a month [104]. At the same tme, the presence of CH_2 or CMe_2 linker between the amide and pyridine groups leads to a significant decrease in the stability of bis(alkyl) complexes with *N,C,C,N*-amidopyridinates. Another factor that determines the stability of bis(alkyl) complexes with *N,C,C,N*-amidopyridine ligands is the existence of substituents at the sixth position of the pyridyl moiety. Rare-earth bis(alkyl) derivatives were isolated only in the case of unsubstituted amidopyridinate ligands (**250–252**) (Fig. 17) [109]. The use of ligands bearing additional substituents at the mentioned position led to the intramolecular C–H bond activation, resulting in alkyl-aryl (**253**) [110], alkyl-benzyl (**254**) [110], and alkyl-hetaryl (**255–258**) [111, 112] complexes and $SiMe_4$ (Fig. 17).
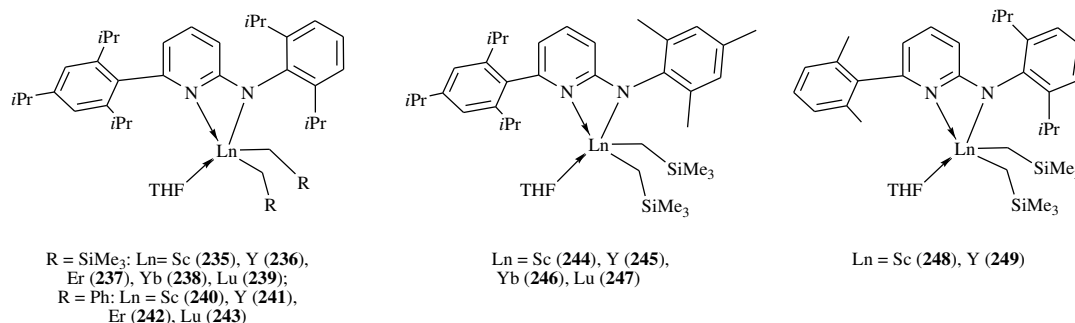
R^1 = Ph, R = CH_2SiMe_3: Ln = Sc, n = 1 (**229**);
Ln = Y, n = 2 (**230**); Ln = Lu, n = 1 (**231**);
R^1 = $CH_2C_6H_4NMe_2$-*o*, R = CH_2SiMe_3, Ln = Lu, n = 1 (**232**);
R^1 = R = CH_2SiMe_3, Ln = Lu, n = 1 (**233**);
R^1 = R = $CH_2C_6H_4NMe_2$-*o*, Ln = Lu, n = 0 (**234**)

Scheme 31

R = $SiMe_3$: Ln= Sc (**235**), Y (**236**),
Er (**237**), Yb (**238**), Lu (**239**);
R = Ph: Ln = Sc (**240**), Y (**241**),
Er (**242**), Lu (**243**)

Ln = Sc (**244**), Y (**245**),
Yb (**246**), Lu (**247**)

Ln = Sc (**248**), Y (**249**)

Figure 16

Ln = Sc (**250**), Y (**251**), Lu (**252**) **253** **254** E = O (**255**), S (**256**) R = H (**257**), Et (**258**)

Figure 17

Ln = Y (**259**), Er (**260**), Yb (**261**), Lu (**262**)

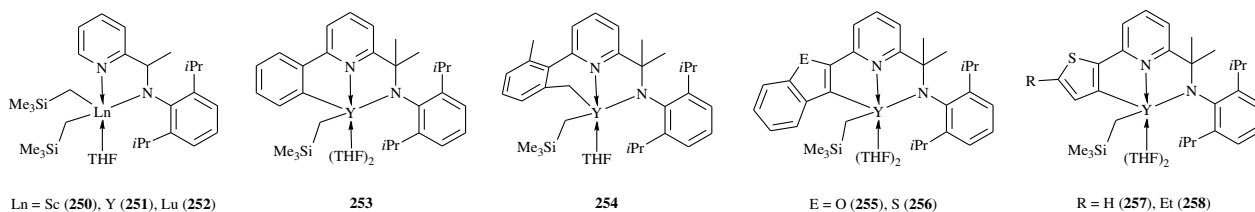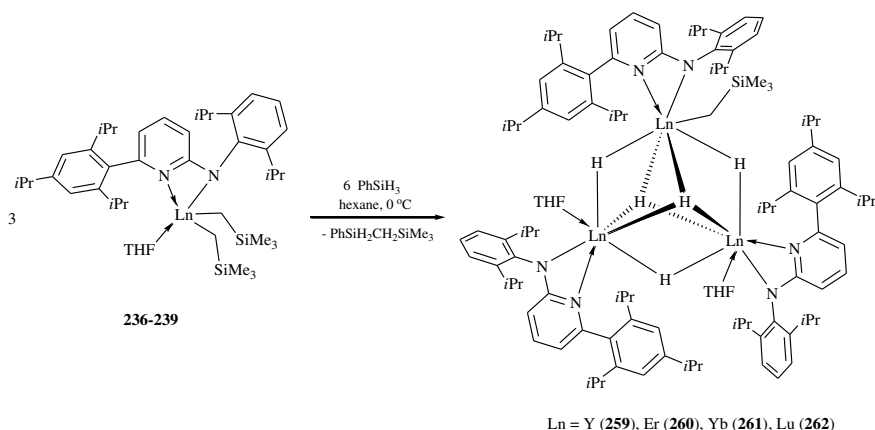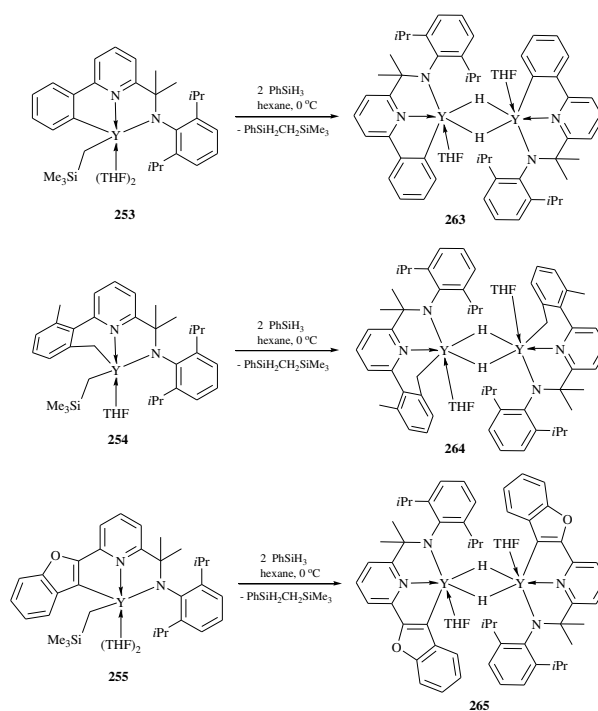**Scheme 32**

Compounds **236–239** undergo hydrogenation upon treatment with PhSiH$_3$ (1:2 molar ratio, 0 °C, hexane) and H$_2$ (P = 5 atm, 15 °C, 24 h), giving rise to trinuclear alkyl hydride complexes **259–262** (Scheme 32) [104, 107].

The selective σ-bond metathesis of Y-CH$_2$SiMe$_3$ was observed in the reaction of compounds **253–255** containing two different Y–C bonds with PhSiH$_3$ (1:2 molar ratio). The corresponding aryl-hydride (**263**), benzyl-hydride (**264**), and heteroaryl-hydride (**265**) complexes were obtained in high yields (Scheme 33) [110, 111]. The second Y–C bond (aryl, benzyl, hetaryl) remained intact even in the presence of a tenfold molar excess of PhSiH$_3$.

Rare-earth bis(alkyl) complexes with bulky amidopyridine ligands **266–269** were synthesized by the reactions of the tris(alkyl) derivatives with equimolar amounts of the corresponding aminopyridines (Fig. 18) [113]. According to the XRD data, complex **268** has distorted trigonal bipyramidal geometry.

A bidentate monoanionic amido-imine ligand system was generated by the reaction of tris(alkyl) complexes Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) with diimines 2,6-R$_2$C$_6$H$_3$N=CHCH=NC$_6$H$_3$R$_2$-2,6 (R = Me, *i*Pr). Bis(alkyl) derivatives [2,6-R$_2$C$_6$H$_3$NCH$_2$C(CH$_2$SiMe$_3$)=NC$_6$H$_3$R$_2$-2,6]Ln(CH$_2$SiMe$_3$)$_2$(THF) (R = Me, Ln = Sc (**270**); R = Me, Ln = Y (**271**); R = Me, Ln = Lu (**272**); R = *i*Pr, Ln = Sc (**273**), R = *i*Pr, Ln = Y (**274**); R = *i*Pr, Ln = Lu (**275**)) (Scheme 34) [114, 115] were derived from the selective transfer of one alkyl group from the rare-earth metal atom to one of two C=N bonds followed by the intramolecular hydrogen migration. The interaction between less bulky diimine 4-MeC$_6$H$_4$N=CHCH=NC$_6$H$_4$Me-4 with Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ led to the alkylation of both C=N bonds, resulting in diamide alkyl complex [4-MeC$_6$H$_4$NCH(CH$_2$SiMe$_3$)]$_2$ScCH$_2$SiMe$_3$(THF)$_2$ (**276**) [114].

253 → **263**

254 → **264**

255 → **265**

Scheme 33

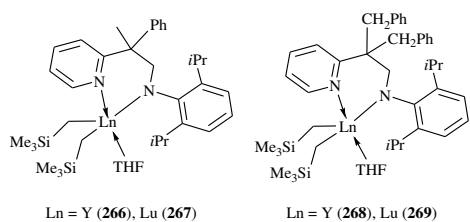Ln = Y (**266**), Lu (**267**)   Ln = Y (**268**), Lu (**269**)

Figure 18

Heating of complex **273** in hexane at 70 °C promoted the intramolecular activation of one of the methyl C–H bonds in the isopropyl group of the ligand and afforded heteroalkyl complex [2-(CH$_2$CH(Me))-6-iPrC$_6$H$_3$-N=C(CH$_2$SiMe$_3$)-CH$_2$-NC$_6$H$_3$$iPr_2$-2,6]ScCH$_2$SiMe$_3$(THF) (**277**) (Scheme 35) [114].

Bis(alkyl) yttrium and lutetium species bearing an amido-imino ligand system [(2,6- iPr$_2$C$_6$H$_3$)N=C(Me)C(=CH$_2$)N(C$_6$H$_3$-2,6-iPr$_2$)]Ln(CH$_2$SiMe$_3$)$_2$THF (Ln = Y (**278**), Lu (**279**)) were synthesized by the reactions of amido lithium derivative [(2,6-iPr$_2$C$_6$H$_3$)N=C(Me)C(=CH$_2$)N(C$_6$H$_3$-2,6-iPr$_2$)]Li(OEt$_2$) [116] with equimolar amounts of anhydrous LnCl$_3$ (Ln = Y, Lu) followed by the alkylation with LiCH$_2$SiMe$_3$ (Scheme 36) [117].

Treatment of bis(alkyl) yttrium complex **278** with an excess of DME in hexane resulted in the cleavage of the C–O bond of DME and the loss of one alkyl group, affording methoxy-alkyl yttrium species {[(2,6-iPr$_2$C$_6$H$_3$)N=C(Me)C(=CH$_2$)N(C$_6$H$_3$-2,6-iPr$_2$)]Y(CH$_2$SiMe$_3$)-(μ-OMe)}$_2$ (**280**) (Scheme 37) [117].

Bis(alkyl) rare-earth complexes [2-(2,6-Me$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (Ln = Sc, n = 1 (**281**); Lu, n = 2 (**282**)) [118] were synthesized by the reactions of 2-(iminomethyl)pyrrole with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y) (Scheme 38). The most sterically hindered 2-(iminomethyl)pyrrole with 2,6-diisopropylphenyl substituents afforded bis(pyrrolyl-aldiminate) mono(alkyl) complexes of lanthanides [2-(2,6-iPr$_2$C$_6$H$_3$N=CH)-C$_4$H$_3$N]$_2$Ln(CH$_2$SiMe$_3$)(THF) (Ln = Sc (**283**), Lu (**284**)) [118]. The use of tBu-substituted 2-(imino)pyrrole 2-(2,6-iPr$_2$C$_6$H$_3$N=CH)C$_4$H$_2$NHtBu instead of 2-(2,6-iPr$_2$C$_6$H$_3$N=CH)C$_4$H$_3$N in the reaction with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_n$ (Ln = Y, n = 2; Ln = Sm, n = 3) led to the formation of bis(alkyl) complexes 2-(2,6-iPr$_2$C$_6$H$_3$N=CH)-5-tBuC$_4$H$_2$N]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_2$ (Ln = Y (**285**); Sm (**286**)) (Scheme 38) [119].

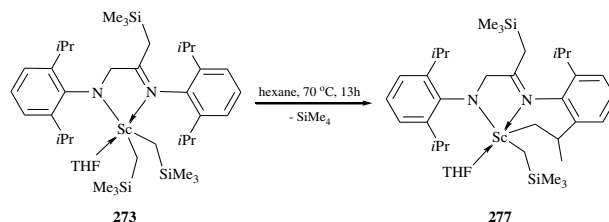However, in the case of yttrium, a bimetallic pyrrolyl-aldiminate monoalkyl complex (**287**) was obtained in the reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with 2-[(N-2,6-diisopropylphenyl)iminomethyl)]pyrrole (Scheme 39) [120]. This reaction was accompanied by the deprotonation of the iminopyrrole by the alkyl group of the tris(alkyl) derivative, while the C=N bond inserted into the second YCH$_2$SiMe$_3$ bond. The dianionic ligand appeared to be bound with two metal centers in a η^5/η^1:κ^1-mode [120]. A similar transformation of the ligand was observed in the reaction of iminopyrrole 2-(2-CH$_3$OC$_6$H$_3$N=CH)C$_4$H$_3$NH with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$, resulting in bimetallic pyrrolyl-aldiminate monoalkyl complexes of [{2-(2-CH$_3$OC$_6$H$_3$NCH(CH$_2$SiMe$_2$))C$_4$H$_3$N}LnCH$_2$SiMe$_3$]$_2$ (Ln = Y, Lu) [121].

The interaction between Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and 2-dimethylaminomethylpyrrole yielded bimetallic bis(alkyl) complexes [(2-(Me$_2$NCH$_2$)-C$_4$H$_3$N)Ln(CH$_2$SiMe$_3$)$_2$]$_2$ (Ln = Sc (**288**), Y (**289**), Lu (**290**)) (Scheme 40) [118].

Bidentate *N*-R-quinolinyl-8-amide ligands (R = Ph, C$_6$H$_3$Me$_2$-2,6, C$_6$H$_2$Me$_3$-2,4,6, C$_6$H$_3$Et$_2$-2,6, C$_6$H$_3$$iPr_2$-2,6) were successfully used for the synthesis of extremely stable bis(alkyl) derivatives of rare-earth elements (Scheme 41) [122, 123]. Complexes **291**–**299** were obtained in good yields by the reactions of aminoquinolines with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu). However, an attempt to synthesize a neodymium analog by the reaction of tris(alkyl) derivative

R = Me: Ln = Sc (**270**), Y (**271**), Lu (**272**);
R = iPr: Ln = Sc (**273**), Y (**274**), Lu (**275**)

Scheme 34

Scheme 35

Ln = Y (**278**), Lu (**279**)

Scheme 36

Scheme 37

R' = H, R = Me:
Ln = Sc, n = 1 (**281**); Ln = Lu, n = 2 (**282**);
R' = tBu, R = iPr:
Ln = Y, n = 2 (**285**); Ln = Sm, n = 2 (**286**)

Scheme 38

287
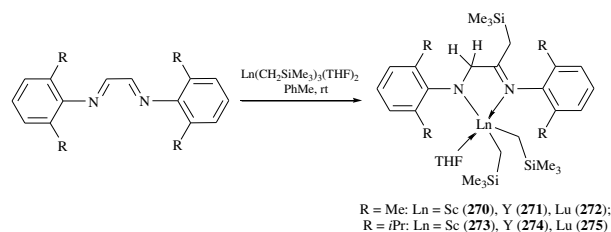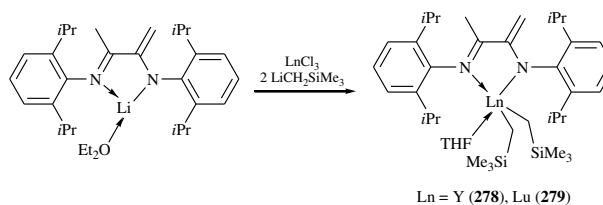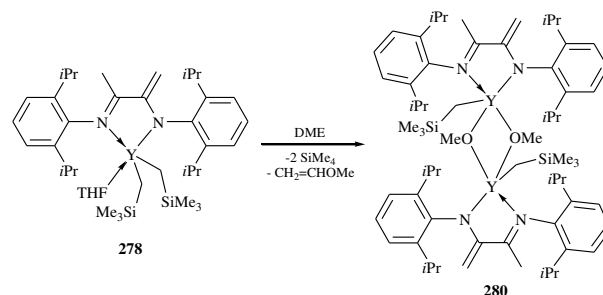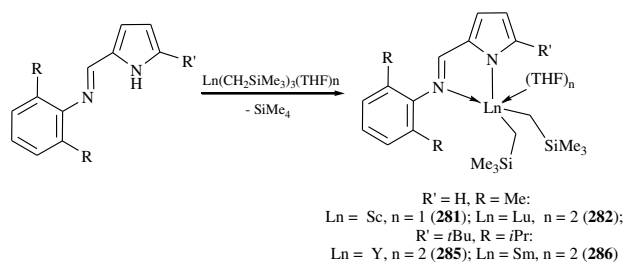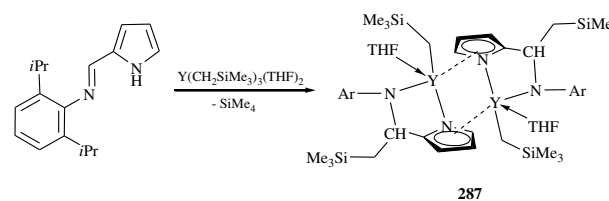
Scheme 39

Nd(CH$_2$SiMe$_3$)$_3$(THF)$_n$ with R-quinolinyl-8-amine (R = C$_6$H$_3$iPr$_2$-2,6) afforded mono(alky) bis(amide) complex L$_2$Nd(CH$_2$SiMe$_3$)(THF) (**300**) [123]. Cationic alkyl complex [LSc(CH$_2$SiMe$_3$)(DME)$_2$][B(C$_6$F$_5$)$_4$] (L = *N*-2,6-Me$_2$C$_6$H$_3$-quinolinyl-8-amide) was obtained upon treatment of compound **291** with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] [122].

A wide range of rare-earth (Sc, Y, La, Ce, Er) hydrocarbyl species coordinated by β-diketiminate ligands RNC(R')CHC(R')NR (R= C$_6$H$_3$iPr$_2$-2,6, C$_6$H$_3$Me$_2$-2,6, SiMe$_3$; R' = CH$_3$, *t*Bu, Ph) have been published to date [93, 124–128]. Lappert and co-workers were the first who synthesized and structurally characterized a bis(alkyl) complex of lanthanide stabilized by β-diketiminate ligand {CH[C(Ph)NSiMe$_3$]$_2$}-Ce[CH(SiMe$_3$)$_2$]$_2$ (**301**) [124]. This compound was the only product isolated from the alkylation of bis(β-diketiminate) chloride complex {CH[C(Ph)NSiMe$_3$]$_2$}$_2$CeCl with one or two equivalents of Li[CH(SiMe$_3$)$_2$]$_2$ (Scheme 42).
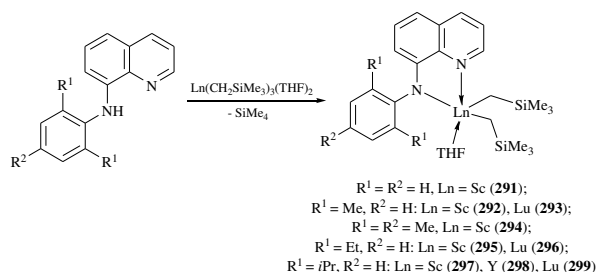
A series of bis(alkyl) complexes of Sc, Y, La, and Er were synthesized by the alkane elimination or the reactions with alkyllithium reagents. Bis(alkyl) scandium complexes {CH[C(R)NR']$_2$}ScR''$_2$(THF)$_n$ (**302–310**, R = Me, *t*Bu; R' = C$_6$H$_3$iPr$_2$-2,6; R'' = Me, Et, CH$_2$Ph, CH$_2$CMe$_3$, CH$_2$SiMe$_3$) were obtained upon treatment of parent dichloride complexes {CH[C(R)NR']$_2$}ScCl$_2$(THF)$_n$ with two equivalents of organolithium or organomagnesium compounds in moderate and good yields (Fig. 19) [125]. Most of the alkyl scandium compounds stabilized by the *t*Bu-substituted β-diketiminate ligand were isolated as solvent-free four-coordinate complexes. Only dimethyl derivative **302**, containing Me-substituted β-diketiminate ligand, has a THF molecule coordinated to the metal center (Fig. 19). Dibenzyl (**303** and **308**), bis(neopentyl) (**304** and **309**), and bis(trimethyl)silylmethyl derivatives (**305** and **310**) have sufficient volumes to exclude the coordination of THF. In addition, the use of this *t*Bu-substituted ligand enabled the isolation of diethyl complex **310**.

Four-coordinated bis(alkyl) complexes of scandium **303–310** and **314** are not thermally stable in benzene. In all cases there were observed the activation of the C–H bond in the isopropyl group of C$_6$H$_3$iPr$_2$-2,6 fragment and the formation of the R–H bond [125].

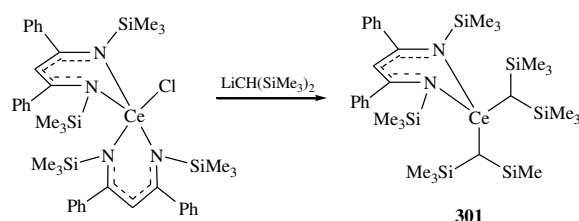Yttrium complex {CH[C(Me)N(C$_6$H$_3$Me$_2$-2,6)]$_2$}Y(CH$_2$SiMe$_3$)$_2$(THF) (**311**) (Fig. 19) was synthesized by the reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with a β-diketimine [126]. At the same time, compounds {CH[C(R)N(C$_6$H$_3$iPr$_2$-2,6)]$_2$}YR'$_2$(THF) (**312–317**; R = Me, *t*Bu; R' = Me, CH$_2$Ph, CH$_2$SiMe$_2$Ph) were obtained by the alkylation of the starting diiodides with organolithium or organopotassium reagents (Fig. 19) [127]. Similarly to scandium compounds, complexes stabilized with the less bulky Me-substituted ligand can contain THF molecules in the metal coordination sphere during the alkylation process (for **313**). Complexes **315–317** with a *t*Bu-substituted β-diketiminate ligand did not contain the coordinated Lewis-base molecules even when THF was used as a solvent. More bulky CH$_2$SiMe$_2$Ph groups excluded the coordination of THF molecules on the metal center (solvent-free complexes **314** and **317**). Bis(alkyl) yttrium compounds showed moderate thermal stability in aromatic solvents. They undergo intramolecular C–H bond activation of the methyl group in 2,6-

Ln = Sc (**288**), Y (**289**), Lu (**290**)

Scheme 40

R^1 = R^2 = H, Ln = Sc (**291**);
R^1 = Me, R^2 = H: Ln = Sc (**292**), Lu (**293**);
R^1 = R^2 = Me, Ln = Sc (**294**);
R^1 = Et, R^2 = H: Ln = Sc (**295**), Lu (**296**);
R^1 = iPr, R^2 = H: Ln = Sc (**297**), Y (**298**), Lu (**299**)
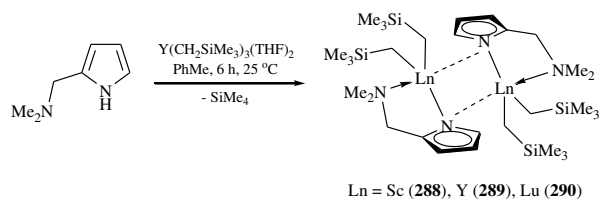
Scheme 41

301

Scheme 42

Ln = Sc

Ar = C$_6$H$_3$iPr$_2$-2,6
R = R' = Me: n = 1 (**302a**), 0 (**302b**);
R = Me, R' = CH$_2$Ph, n = 0 (**303**);
R = Me, R' = CH$_2$CMe$_3$, n = 0 (**304**);
R = Me, R' = CH$_2$SiMe$_3$, n = 0 (**305**);
R = *t*Bu, R' = Me, n = 0 (**306**);
R = *t*Bu, R' = Et, n = 0 (**307**);
R = *t*Bu, R' = CH$_2$Ph, n = 0 (**308**);
R = *t*Bu, R' = CH$_2$CMe$_3$, n = 0 (**309**);
R = *t*Bu, R' = CH$_2$SiMe$_3$, n = 0 (**310**)

Ln = Y

Ar = C$_6$H$_3$Me$_2$-2,6:
R = Me, R' = CH$_2$SiMe$_3$, n = 1 (**311**);
Ar = C$_6$H$_3$iPr$_2$-2,6:
R = R' = Me, n = 0 (**312**);
R = Me, R' = CH$_2$Ph, n = 1 (**313**);
R = Me, R' = CH$_2$SiMe$_2$Ph, n = 0 (**314**);
R = *t*Bu, R' = Me, n = 0 (**315**);
R = *t*Bu, R' = CH$_2$Ph, n = 0 (**316**);
R = *t*Bu, R' = CH$_2$SiMe$_2$Ph, n = 0 (**317**)

Ln = La

Ar = C$_6$H$_3$iPr$_2$-2,6, R = Me,
R' = CH$_2$Ph, n = 1 (**318**)

Ln = Er

Ar = C$_6$H$_3$iPr$_2$-2,6, R = Me,
R' = CH$_2$SiMe$_3$, n = 0 (**319**)

Figure 19

*i*Pr$_2$C$_6$H$_3$ fragment followed by the elimination of an alkane [127].

In addition, β-diketiminate ligands proved to be convenient coordination environments for the synthesis of bis(alkyl) complexes of lanthanides with large ionic radii. Lanthanum
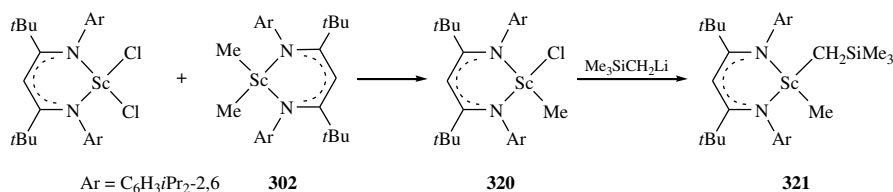
Scheme 43

complex {HC[C(Me)NC$_6$H$_3$iPr$_2$-2,6]$_2$}La(CH$_2$Ph)$_2$(THF) (**318**) (Fig. 19) was synthesized by the interaction of LaBr$_3$(THF)$_4$ and K{HC[C(Me)NC$_6$H$_3$iPr$_2$-2,6]$_2$} with subsequent treatment with two equivalents of PhCH$_2$K (Fig. 19) [93]. The reaction of dimeric chloride complex {HC[C(Me)NC$_6$H$_3$iPr$_2$-2,6]$_2$}ErCl(μ-Cl)$_3$Er{HC[C(Me)NC$_6$H$_3$iPr$_2$-2,6]$_2$}(THF) with four equivalents of LiCH$_2$SiMe$_3$ resulted in a solvent-free four-coordinate bis(alkyl) complex {HC[C(Me)NC$_6$H$_3$iPr$_2$-2,6]$_2$}Er(CH$_2$SiMe$_3$)$_2$ (**319**) (Fig. 19) [128].

Heteroalkyl scandium derivative {CH[C(tBu)N(C$_6$H$_3$iPr$_2$-2,6)]$_2$}Sc(CH$_3$)CH$_2$SiMe$_3$ (**321**) was obtained by the exchange reaction between equimolar amounts of the corresponding dichloride and dimethyl complexes followed by the treatment with LiCH$_2$SiMe$_3$ (Scheme 43) [125].

W. E. Piers *et al*. proposed and successfully implemented a "remote steric bulk" strategy for stabilization of low-coordinate bis(alkyl) scandium complexes (**322–325**) [127]. A significant improvement in the thermal stabilities of neutral bis(alkyl) and cationic alkyl scandium complexes was achieved owing to the use of a new β-diketiminate ligand containing bulky *ortho*-substituted aryl fragments at the nitrogen atoms (Fig. 20) [129].

Scandium complexes **315–318** appeared to be much more thermally stable than the bis(alkyl) derivatives containing {HC[C(Me)NC$_6$H$_3$iPr$_2$-2,6]$_2$} ligands (**302–310**). For example, complexes **305** and **307** begin to decompose at 60 °C in 15 min, while compounds **322–325** remain intact upon heating at 100 °C. The decomposition of these complexes was detected only after heating at 120 °C for 5 h [129].

Potentially tetradentate bis(β-diketiminate) ligands *m*-C$_6$H$_4$[NC(Me)CHC(Me)NHC$_6$H$_3$R$_2$-2,6]$_2$ (R = Me, Et, iPr) with a *meta*-phenylene bridge between two β-diketiminate fragments were used in the reactions with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu), which resulted in binuclear bis(alkyl) complexes *m*-C$_6$H$_4${[NC(Me)CHC(Me)NC$_6$H$_3$R$_2$-2,6]Ln(CH$_2$SiMe$_3$)$_2$-(THF)$_n$}$_2$ (R = Me, Ln = Y, n = 1 (**326**); R = Et, Ln = Sc, n = 0 (**327**); R = Et, Ln = Y, n = 1 (**328**); R = Et, Ln = Lu, n = 1 (**329**); R = iPr, Ln = Y, n = 1 (**330**)) (Fig. 21) [130]. According to the X-ray analysis data, each β-diketiminate fragment is coordinated to the metal center in a κ^2-*N,N*-fashion.

Bis(alkyl) scandium derivatives **302–306** were used for the synthesis of cationic alkyl complexes [131–135]. The reaction of scandium dibenzylic complex **303** with the Lewis acid B(C$_6$F$_5$)$_3$ resulted in separated ion pair [{HC(C(Me)NC$_6$H$_3$iPr$_2$-2,6)$_2$}Sc(CH$_2$Ph)]$^+$[PhCH$_2$B(C$_6$F$_5$)$_3$]$^-$ (**331**) (Scheme 44) in which the aromatic ring of the benzyl group is coordinated to the metal atom in a η^6-fashion [131].

The structures of cationic alkyl scandium complexes depend on the molar ratio of the reagents. Thus, the reaction of scandium dimethyl derivative **306** with B(C$_6$F$_5$)$_3$ in a 1:0.5 ratio led to the formation of binuclear cationic complex [{{HC(C(tBu)NC$_6$H$_3$iPr$_2$-2,6)$_2$]ScMe}$_2$(μ^2-Me)]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$
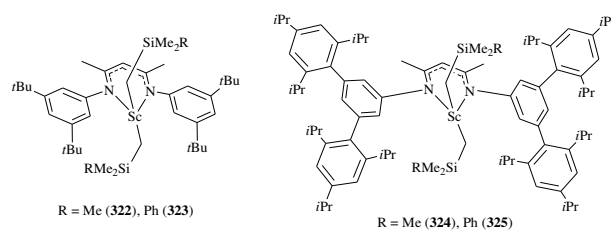
Figure 20
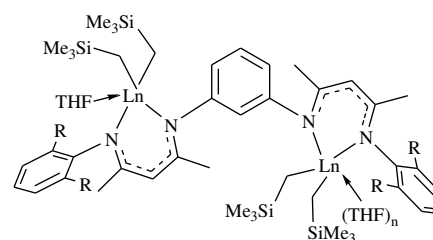
R = Me, Ln = Y, n = 1 (**326**),
R = Et, Ln = Sc, n = 0 (**327**),
R = Et, Ln = Y, n = 1 (**328**),
R = Et, Ln = Lu, n = 1 (**329**),
R = iPr, Ln = Y, n = 1 (**330**)

Figure 21
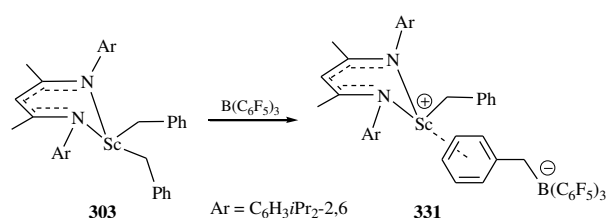
Scheme 44

(**332**) (Scheme 45). In compound **332** two metal ions are connected by one μ-bridging methyl group [132]. Monomeric complex [{HC(C(tBu)NC$_6$H$_3$iPr$_2$-2,6)$_2$}ScMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**333**) was obtained by the reaction of equimolar amounts of **306** and B(C$_6$F$_5$)$_3$ (Scheme 45). The counterions are bound by one μ-bridging methyl group and the weak interaction between Sc and F atom located at the *ortho*-position of one of C$_6$F$_5$ rings [132]. Cationic complex [{HC(C(tBu)NC$_6$H$_3$iPr$_2$-2,6)$_2$}Sc]$^{2+}$[MeB(C$_6$F$_5$)$_3$]$^-_2$ (**334**) was obtained upon treatment of compound **306** with two equivalents of B(C$_6$F$_5$)$_3$ (Scheme 45) [132].

The reaction of dimethyl complex **302b** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in a solution of bromobenzene led to solvent-separated ion pair [{HC(C(Me)NC$_6$H$_3$iPr$_2$-2,6)$_2$}ScMe(C$_6$H$_5$Br)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**335**) (Scheme 46) [133]. Bromobenzene is coordinated to the Sc atom in a η^6-mode; it can be easily replaced by other highly basic arenes (C$_6$H$_6$, C$_6$H$_5$Me, C$_6$H$_3$Me$_3$) [133, 134].

Scheme 45

Scheme 46

R = Me (**305**), *t*Bu (**310**)   R = Me (**336**), *t*Bu (**337**)

Scheme 47

338

Scheme 48

R = Me (**339**), Ph (**340**)
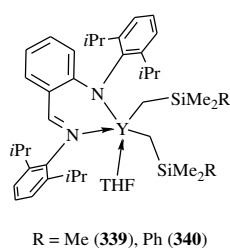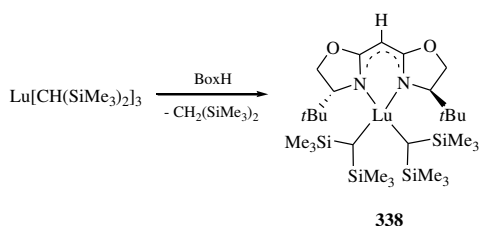
Figure 22

Complexes **305** and **310** react with *n*BuP=Te *via* Te insertion into the Sc–C bond to form bis(tellurate) derivatives {HC[C(R)NC$_6$H$_3$*i*Pr$_2$-2,6]$_2$}Sc(TeCH$_2$SiMe$_3$)$_2$ (R = Me (**336**), *t*Bu (**337**)) (Scheme 47) [135].

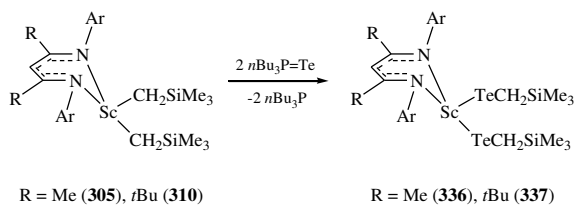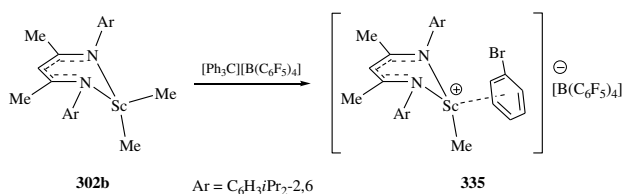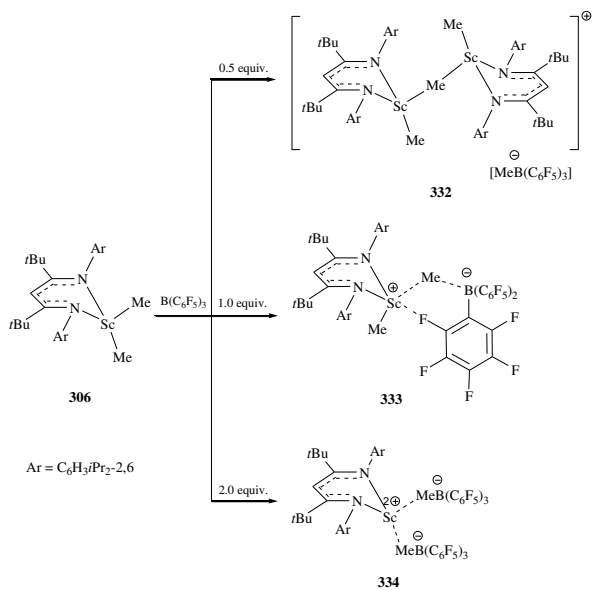A chiral bis(oxazoline) ligand (Box) containing a similar β-diketimine skeleton was successfully used to synthesize bis(alkyl) lutetium complex [(4S)-*t*BuBox]Lu[CH(SiMe$_3$)$_2$]$_2$ (**338**) (Scheme 48) [136]. The structure of compound **338** was confirmed by XRD.

Bis(alkyl) yttrium complexes **339** and **340** were obtained by the reaction of YCl$_3$ with lithium anilide followed by the alkylation with two equivalents of RSiMe$_2$CH$_2$Li (R = Me, Ph) (Fig. 22) [137].

The reactions of equimolar amounts of 7-{(NAr)iminomethyl)}indoles (Ar = C$_6$H$_3$Me$_2$-2,6, C$_6$H$_3$*i*Pr$_2$-2,6) and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Lu) afforded bis(alkyl) complexes [7-(2,6-R$_2$C$_6$H$_3$NCH)C$_8$H$_5$N]Ln(CH$_2$SiMe$_3$)$_2$(THF) (R = Me, Ln = Sc (**341**); R = Me, Ln = Lu (**342**); R = *i*Pr, Ln = Sc (**343**); R = *i*Pr, Ln = Lu (**344**)) (Fig. 23) [138]. The structure of lutetium complex **341** was confirmed by X-ray crystallography. Treatment of compound **341** with two equivalents of carbodiimide *i*PrN=C=N*i*Pr yielded bis(amidinate) complex 7-(2,6-Me$_2$-C$_6$H$_3$NCH)C$_8$H$_5$N]Lu[(*i*PrN)$_2$CCH$_2$SiMe$_3$]$_2$ (**345**) [138].

The interaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with aminopyridines 6-R-C$_5$H$_3$N-2[CHC(Me)NH(C$_6$H$_3$*i*Pr$_2$-2,6)] (R = SiMe$_3$, Ph) did not lead to the expected bis(alkyl) derivatives, giving rise to mono(alkyl) complexes **346** and **347** containing new tridentate pyridyl-1-azaallyl dianionic ligands (Fig. 24) [139]. This indicates that the deprotanation of a β-diketimine framework was accompanied by the activation of the C(sp^3)–H (**346**) or C(sp^2)–H (**347**) bond of SiMe$_3$ or Ph substituent, respectively. In addition, the use of less bulky aminopyridines 6-Me-C$_5$H$_3$N-2[CHC(R')NH(C$_6$H$_3$R''$_2$-2,6)] (R' = R'' = Me; R' = Ph, R'' = Me; R' = Ph, R'' = *i*Pr) with methyl groups at the sixth position of the pyridine ring in reactions with Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ led to the formation of a mixture of products [139].
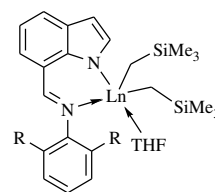
R = Me: Ln = Sc (**341**), Lu (**342**);
R = *i*Pr: Ln = Sc (**343**), Lu (**344**)

Figure 23

346   **347**

Figure 24

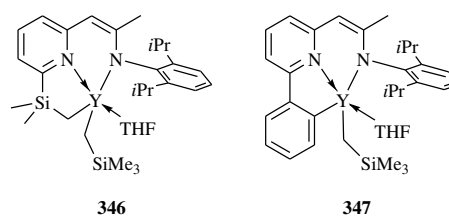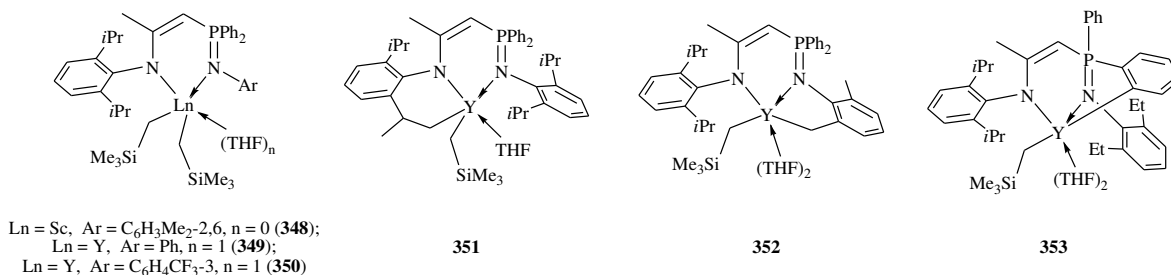Ln = Sc, Ar = C$_6$H$_3$Me$_2$-2,6, n = 0 (**348**);
Ln = Y, Ar = Ph, n = 1 (**349**);
Ln = Y, Ar = C$_6$H$_4$CF$_3$-3, n = 1 (**350**)

351

352

353

Figure 25

A series of phosphiniminoamines (2,6-iPr$_2$-C$_6$H$_3$NH)C(Me)CHPPh$_2$(NAr) (Ar = C$_6$H$_3$$iPr_2$-2,6, C$_6H_3Et_2$-2,6, C$_6H_3Me_2$-2,6, Ph, C$_6H_4CF_3$-3) were used in the reactions of alkane elimination with Ln(CH$_2$SiMe$_3$)$_2$(THF)$_2$. The interaction of Sc(CH$_2$SiMe$_3$)$_2$(THF)$_2$ with (2,6-iPr$_2$C$_6$H$_3$NH)C(Me)CHPPh$_2$(NC$_6$H$_3$Me$_2$-2,6) resulted in solvent-free complex (2,6-iPr$_2$C$_6$H$_3$N)C(Me)CHPPh$_2$(NC$_6$H$_3$Me$_2$-2,6)Sc(CH$_2$SiMe$_3$)$_2$ (**348**) (Fig. 25) [140]. Li *et al.* demonstrated that the reaction of Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ with phosphiniminoamines (2,6-iPr$_2$C$_6$H$_3$NH)C(Me)CHPPh$_2$(NAr) strongly depends on the nature of the substituent at the imine nitrogen atom [141]. Bis(alkyl) complexes [2,6-iPr$_2$-C$_6$H$_3$N)C(Me)CHPPh$_2$(NR)]Y(CH$_2$SiMe$_3$)$_2$(THF) (R = Ph (**349**), C$_6$H$_4$CF$_3$-3 (**350**) were obtained from the reactions of Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ with (2,6-iPr$_2$C$_6$H$_3$NH)C(Me)CHPPh$_2$(NAr) (Ar = Ph, C$_6$H$_4$CF$_3$-3) (Fig. 25) [141]. In the case of phosphiniminoamines (2,6-iPr$_2$C$_6$H$_3$NH)C(Me)CHPPh$_2$(NAr) (Ar = C$_6$H$_3$$iPr_2$-2,6, C$_6H_3Me_2$-2,6), the elimination of alkane was accompanied by the activation of the C–H bond of the methyl group in C$_6$H$_3$$iPr_2$-2,6 or C$_6H_3Me_2$-2,6 fragments (**351** and **352**) (Fig. 25) [141]. Moreover, (2,6-iPr$_2$C$_6$H$_3$NH)C(Me)CHPPh$_2$(NC$_6$H$_3$Et$_2$-2,6) underwent the C–H bond activation of one of the phenyl substituents in PPh$_2$ group (**353**) (Fig. 25) [141].

Piers *et al.* described the syntheses, structures, and stabilities of a series of dimethyl scandium complexes stabilized by anilido-phosphinimide *N,N*-donor ligands [1-(2,6-iPr$_2$C$_6$H$_3$N)-2-(PPh$_2$=NAr)C$_6$H$_4$]ScMe$_2$ (Ar = C$_6$H$_2$Me$_3$-2,4,6 (**354**), C$_6$H$_4$$i$Pr-2 (**355**), C$_6H_3$$iPr_2$-2,6 (**356**)) (Fig. 26) [142]. Scandium complex with trimethylsilylmethyl groups **357** was synthesized by the reaction of equimolar amounts of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ and [1-(PhCH$_2$NH)-2-(PPh$_2$=NC$_6$H$_3$Et$_2$-2,6)C$_6$H$_4$] [142]. Unlike dimethyl derivatives, compound [1-(PhCH$_2$N)-2-(PPh$_2$=NC$_6$H$_3$Et$_2$-2,6)C$_6$H$_4$]Sc(CH$_2$SiMe$_3$)$_2$(THF) (**357**) contains a THF molecule in the metal coordination sphere. Dimethyl complexes **354**–**356** are extremely stable in the crystalline state in an argon atmosphere, although in solution they undergo partial decomposition. Compound **354** bearing mesityl substituents rapidly decomposes at room temperature due to the activation of the methyl C–H bond in the mesityl substituent, resulting in complex **358** (Scheme 49). At the same time, bis(alkyl) derivative **355** does not undergo decomposition even upon heating in C$_6$D$_6$ at 65 °C for 24 h [142].

The use of ligand systems with the phenyl substituents at the phosphorus atom allowed for the preparation of bis(alkyl) scandium derivatives **354**–**356** by the reactions with MeLi. At the same time, ligand [1-(2,6-iPr$_2$C$_6$H$_3$N)-2-(PMe$_2$=NC$_6$H$_3$$iPr_2$-2,6)C$_6H_4$]$^-$ containing PMe$_2$ group afforded metallated product

359 (Fig. 27) [142]. Complex **359** is a dimer in which two scandium atoms are connected by μ-bridging methyl groups.

The interaction of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Y, Lu) with aniline-phosphinimine [1-(2,6-iPr$_2$C$_6$H$_3$NH)-2-(PPh$_2$=NC$_6$H$_2$Me$_3$-2,4,6)C$_6$H$_4$] was accompanied by the protonation of one Ln–CH$_2$SiMe$_3$ bond as well as the activation of the C–H bond of one of the phenyl substituents in PPh$_2$ groups, which afforded the corresponding alkyl-aryl derivatives (Ln = Y (**360**), Lu (**361**)) (Fig. 28) [143]. Liu *et al.* [143] studied the reactivity of complexes **360** and **361** towards PhSiH$_3$, [Ph$_3$C][B(C$_6$F$_5$)$_4$], and AlMe$_3$ and showed that only the Ln–CH$_2$SiMe$_3$ bond was involved in the reactions, while the Ln–C$_{Phenyl}$ bond remained intact. In contrast, treatment of compound **361** with terminal acetylene PhC≡CH proceeded with the protonolysis of both of the Ln–C bonds and resulted in
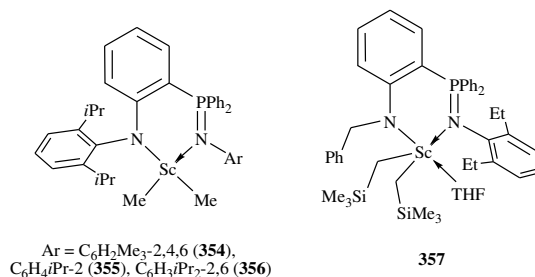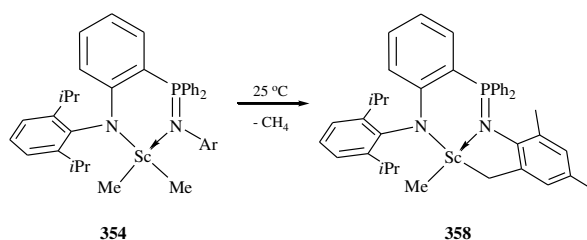

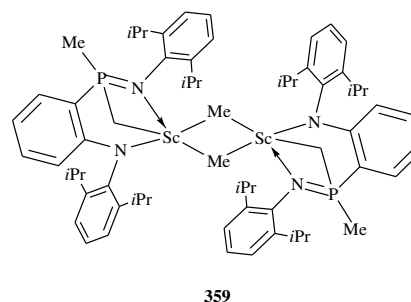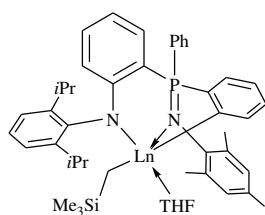Ar = C$_6$H$_2$Me$_3$-2,4,6 (**354**),
C$_6$H$_4$$i$Pr-2 (**355**), C$_6H_3$$iPr_2$-2,6 (**356**)

357

Figure 26

354

25 °C
– CH$_4$

358

Scheme 49

359

Figure 27

bis(acetylide) complex [1-(2,6-*i*Pr$_2$C$_6$H$_3$N)-2-(PPh$_2$=NC$_6$H$_2$Me$_3$-2,4,6)C$_6$H$_4$]Lu(C≡CPh)$_2$(DME) (**362**) [144].

The reactions of analogous thiophenyl-substituted aniline-phosphinimines [1-(MeC$_4$H$_2$SCH$_2$NH)-2-(PPh$_2$=NAr)C$_6$H$_4$] (Ar = C$_6$H$_2$Me$_3$-2,4,6, C$_6$H$_3$Et$_2$-2,6, C$_6$H$_3$*i*Pr$_2$-2,6) with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) furnished the corresponding bis(alkyl) derivatives **363–368** in quantitative yields (Fig. 29) [145]. According to the results of X-ray diffraction studies of complexes **364**, **365**, and **368**, the thiophene sulfur atom is not coordinated to the metal atom in the solid state.

Sulfur-containing ligands have not gained widespread use in the chemistry of organic derivatives of rare-earth elements due to very weak binding between sulfur and lanthanides compared to the Ln–N, Ln–O, and Ln–P bonds. There are only a few examples of the application of sulfur-containing ligands in the synthesis of bis(alkyl) rare-earth complexes. Cui *et al*. investigated the interaction of thiophene-amines 2,6-*i*Pr$_2$C$_6$H$_3$NHCH$_2$(C$_4$H$_3$S-2) with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) [146]. In the case of yttrium and lutetium, the reactions led to the formation of alkyl-heteroaryl complexes [2,6-*i*Pr$_2$C$_6$H$_3$NCH$_2$(C$_4$H$_3$S-2)]Ln(CH$_2$SiMe$_3$)(THF)$_3$ (Ln = Y (**369**), Lu (**370**)) due to the protonation of the Ln–CH$_2$SiMe$_3$ bond and the activation of the C–H bond in the thiophenyl ring (Scheme 50) [146]. Unexpectedly, despite the ionic radius of Sc, the equimolar reaction of Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with 2,6-*i*Pr$_2$C$_6$H$_3$NHCH$_2$(C$_4$H$_3$S-2) afforded a heteroleptic complex with two coordinated thiophenyl amide ligands [2,6-*i*Pr$_2$C$_6$H$_3$NCH$_2$(C$_4$H$_3$S-2)][2,6-*i*Pr$_2$C$_6$H$_3$NCH$_2$(C$_4$H$_3$S-2)]Sc(THF) (**371**) (Scheme 50). One of the ligands is dianionic and is linked to the scandium ion *via* covalent Sc–C and Sc–N bonds, whereas the second ligand is monoanionic and is coordinated to the metal center through the covalent Sc–N and coordination Sc–S bonds [146].

Scheme 50

3.3. Rare-earth bis(alkyl) complexes with the tridentate *N*-containing ligands

Tris(pyrazolylborates) (Tp$^{R,R'}$) have found wide application as stabilizing ligands in the chemistry of rare-earth elements [147]. The steric properties of these ligand systems can be easily modified by variation of substituents at the third position of the pyrazole rings. Initially, bis(alkyl) derivatives of rare-earth elements containing Tp$^{R,R'}$ ligands were synthesized by the alkane elimination or the exchange reactions with alkyllithium reagents. Yttrium complexes (Tp^{Me2})YR$_2$(THF) (R = Ph (**372**), CH$_2$SiMe$_3$ (**373**) [148], CH$_2$Ph (**374**) [149]) (Scheme 51) were prepared by the alkylation of (Tp^{Me2})YCl$_2$(THF) with LiR (R = Ph, CH$_2$SiMe$_3$) or KR (R = CH$_2$Ph).

Attempts to synthesize analogous scandium complexes by the reactions of (Tp^{Me2})ScCl$_2$(THF) and (Tp^{tBu,Me})ScCl$_2$ with RLi (R = Me, CH$_2$SiMe$_3$, CH(SiMe$_3$)$_2$) led to lithium tris(pyrazolylborates) as the main products. The interaction of HTp$^{R,R'}$ with Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$ allowed for the isolation of the corresponding bis(alkyl) complexes [(Tp^{Me2})Sc(CH$_2$SiMe$_3$)$_2$(THF)] (**375**) and [(Tp^{tBu,Me})Sc(CH$_2$SiMe$_3$)$_2$] (**381**) in high yields (Scheme 52) [150]. This approach was successfully used for the synthesis of bis(alkyl) derivatives of other rare-earth elements (Tp$^{R,R'}$)Ln(CH$_2$SiMe$_3$)$_2$(THF)$_n$ (R = R' = Me, n = 1: Ln = Y (**376**) [149, 151], Yb (**377**), Lu (**378**) [151]; R = R' = *i*Pr, n = 1: Ln = Y (**379**), Lu (**380**) [152]; R = *t*Bu, R' = Me, n = 0: Ln = Y (**382**), Yb (**383**), Lu (**384**) [151]) (Scheme 52).
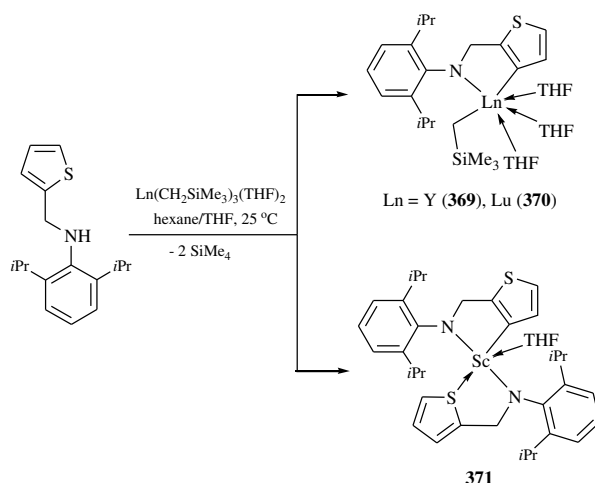
Ln = Y (**360**), Lu (**361**)

Figure 28

Ar = C$_6$H$_2$Me$_3$-2,4,6:
Ln = Sc, n = 1 (**363**); Ln = Lu, n = 1 (**364**);
Ar = C$_6$H$_3$Et$_2$-2,6:
Ln = Sc, n = 1 (**365**); Ln = Y, n = 1 (**366**); Ln = Lu, n = 1 (**367**);
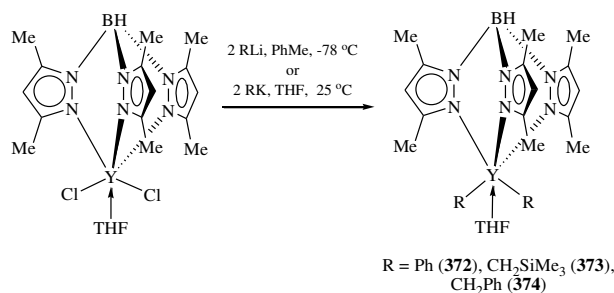Ar = C$_6$H$_3$*i*Pr$_2$-2,6: Ln = Sc, n = 0 (**368**)

Figure 29

R = Ph (**372**), CH$_2$SiMe$_3$ (**373**),
CH$_2$Ph (**374**)

Scheme 51

R = R' = Me, n = 1:
Ln = Sc (**375**), Y (**376**), Yb (**377**), Lu (**378**);
R = R' = *i*Pr, n = 1: Ln = Y (**379**), Lu (**380**);
R = *t*Bu, R' = Me, n = 0:
Ln = Sc (**381**), Y (**382**), Yb (**383**), Lu (**384**)
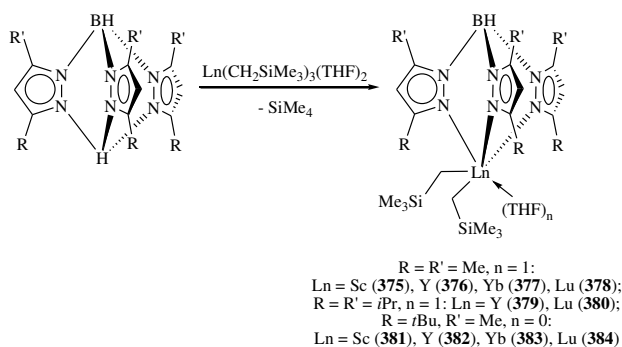
Scheme 52

Scheme 53

An unusual synthetic approach was proposed by Takats *et al.* [151]. They synthesized bis(alkyl) complexes of Y, Yb, and Lu with tris(pyrazolylborate) ligands $(Tp^{R,R'})Ln(CH_2SiMe_3)_2(THF)$ (R = R' = H: Ln = Y (**385**), Yb (**386**), Lu (**387**) [151]; R = R' = Me: Ln = Y (**388**) [151, 152], Yb (**389**), Lu (**390**) [152]) (Scheme 53) by the reactions of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Yb, Lu) with $Tl(Tp^{R,R'})$. In the case of lanthanides having large ionic radii, such as Sm and Nd, treatment of the freshly prepared tris(alkyl) complexes with $Tl(Tp^{Me2})$ afforded bis(alkyl) derivatives $(Tp^{Me2})Ln(CH_2SiMe_3)_2(THF)$ (Ln = Nd (**391**), Sm (**392**)) [151]. Unlike $Tl(Tp^{Me2})$, only bis(alkyl) derivative of lutetium (**393**) was isolated from the reaction with $Tl(Tp^{tBu,Me})$ [151].

It was demonstrated that monomeric low-coordinated lutetium dimethyl complex $(Tp^{tBu,Me})LuMe_2$ (**394**) (Scheme 54) can be obtained by the reaction of $Lu(GaMe_4)_3$ with bulky $(Tp^{tBu,Me})H$ followed by the removal of $GaMe_3$ [153].

It is noteworthy that bulky $Tp^{tBu,Me}$ ligand prevents the coordination of THF molecules to the metal center, resulting in the five-coordinated complexes, whereas Tp^{H2}, Tp^{Me2}, and Tp^{iPr2} afford six-coordinated derivatives with one THF molecule on the lanthanide atom.

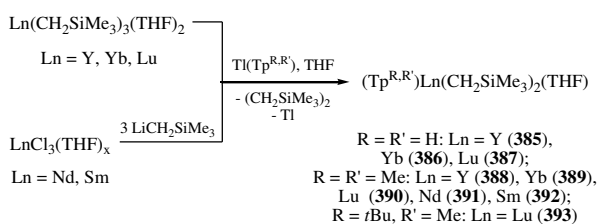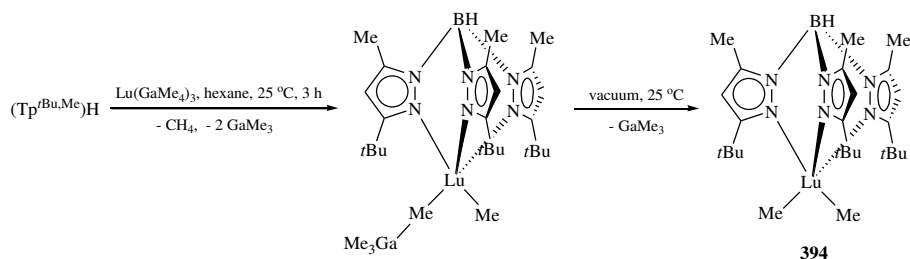Hydride clusters (**395–405**) were synthesized by the reactions of complexes **379–380**, **385–387**, and **388–402** with H_2 at high pressure (75 atm, room temperature) (Scheme 55) [151, 152, 154]. It was noted that the number of metal atoms included into the central framework of a cluster strongly depends on the volume of a tris(pyrazolylborate) ligand. For the less bulky Tp^{H2} ligand, six-nuclear dodecahydride complexes $[(Tp^{H2})LnH_2]_6$ (Ln = Y (**395**) [151], Yb (**396**) [154], Lu (**397**) [151]) were isolated. The use of methyl-substituted tris(pyrazolylborate) led to polyhydride tetrameric clusters $[(Tp^{Me2})LnH_2]_4$ (Ln = Y (**398**) [151], Sm (**399**) [151], Yb (**400**) [154], Lu (**401**) [151], Nd (**402**) [151]) (Scheme 55). In the case of even more bulky Tp^{iPr2}, trinuclear hexahydride complexes $[(Tp^{iPr2})LnH_2]_3$ (Ln = Y (**404**), Lu (**405**) [152]) were obtained

(Scheme 55). The nature of the solvent used at the hydrogenation step also influenced the structures of the resulting clusters. Thus, tetranuclear octahydride clusters **398–402** were formed in toluene, while trinuclear hexahydride complex $[(Tp^{Me2})YH_2]_3(THF)_{2–3}$ (**403**) was isolated from THF [151].

Takats *et. al.* investigated the reactivity of bis(alkyl) complexes **376**, **378**, **382**, and **384** towards substituted acetylenes HC≡CR" (R" = Ph, SiMe3, *t*Bu, Ad, Trit* (Trit* = tris(3,5-di-tert-butylphenyl)methyl)). It was found that the interaction of **376** and **378** with HC≡CR" (R" = Ph, SiMe3, *t*Bu, Ad) leads to the protonolysis of both alkyl groups to form binuclear acetylenide complexes $[(Tp^{Me2})Ln(μ-C≡CR")]_2(μ-R"C_4R")$ (Ln = Y, R" = Ph (**406**), SiMe3 (**407**), *t*Bu (**408**), Ad (**409**); Ln = Lu, R" = Ph (**410**), SiMe3 (**411**), *t*Bu (**412**)) (Scheme 56) with two alkynyl and one R"C=C-C≡CR" bridging ligands [155]. The use of more bulky acetylene HC≡CTrit* in the presence of the chelate Lewis base (2,2'-bipyridyl) excluded alkynyl dimerization and provided monomeric bis(acetylide) complexes $[(Tp^{Me2})Ln(μ-C≡CR")_2(Solv)_n]$ (R" = Trit*, Solv = THF, Ln = Y (**413**), Lu (**414**); R" = *t*Bu, Solv = 2,2'-bipyridine, Ln = Lu (**415**)) (Scheme 56) [155]. The reaction of bis(alkyl) complexes **382** and **384** containing more bulky $Tp^{tBu,Me}$ ligand, with phenylacetylene yielded yttrium and lutetium derivatives with two terminal alkynyl groups $(Tp^{tBu})Ln(C≡CPh)_2$ (Ln = Y (**416**), Lu (**417**)) (Scheme 56) [155].

Yi *et al.* [149] studied the reactivity of dibenzylic yttrium complex **374** towards bis(2,6-diisopropylphenyl)carbodiimide, phenylisocyanate, and phenylisothiocyanate. The interaction of **374** with an equimolar amount of 2,6-*i*Pr2C6H3N=C=NC6H3*i*Pr2-2,6 led to the expected insertion of the carbodiimide into the Y–C bond to form benzyl-amidinate complex $(Tp^{Me2})Y(CH_2Ph)[(2,6-iPr_2C_6H_3N)_2C(CH_2Ph)]$ (**418**) (Scheme 57) [149]. The reaction of **374** with PhN=C=O was accompanied by the addition of the Y–CH2Ph bond to the N=C=O fragment followed by the deprotonation of the leaving benzyl group and the formation of binuclear complex $[(Tp^{Me2})Y(THF)\{μ-η^1:η^3-OC(CHPh)NPh\}\{μ-η^3:η^2-OC(CHPh)NPh\}Y(Tp^{Me2})]$ (**419**) (Scheme 57) [149]. The treatment of **374** with PhN=C=S resulted in the C=S bond cleavage, the elimination of PhN=C(CH2Ph)2, and the formation of cubic cluster $[(Tp^{Me2})Y(μ^3-S)]_4$ (**420**) (Scheme 57) [149].

Hexanuclear 24-membered metallomacrocycle $[(Tp^{Me2})Y(μ-N,C-Im)(η^2-N,C-Im)]_6$ (Im = 1-methylimidazolyl, **421**) was synthesized by the reaction of $(Tp^{Me2})Y(CH_2Ph)_2(THF)$ (**374**) with 1-methylimidazole in a 1:2 ratio (Scheme 58) [156]. This compound resulted from the activation of the C–H bonds at C2 and C5 carbon atoms of the imidazole ring. At the same time, the interaction of **374** with two equivalents of 1-methylbenzimidazole was accompanied by the C–H bond activation and opening of the imidazole ring followed by the formation of the new C–C bond, giving rise to non-classical ionic-type complex $[(Tp^{Me2})Y\{η^3-(N,N,N)-N-(Me)C_6H_4NHCH=C(Ph)-CN(Me)C_6H_4NH\}]$ (**422**) (Scheme 58) [156]. Further studies showed that treatment of complex **374** with one or two equivalents of benzothiazole also proceeds through the opening of the cycle and affords dimeric yttrium complex $\{(Tp^{Me2})Y[μ-η^2:η^1-SC_6H_4N(CH=CHPh)](THF)\}_2$ (**423**) (Scheme 58) [156].

$(Tp^{tBu,Me})H$ $\xrightarrow[\text{– CH}_4, \text{ – 2 GaMe}_3]{\text{Lu(GaMe}_4)_3, \text{ hexane, 25 °C, 3 h}}$

$\xrightarrow[\text{– GaMe}_3]{\text{vacuum, 25 °C}}$

394

Scheme 54

3 $(Tp^{H2})Ln(CH_2SiMe_3)_2(THF)$ $\xrightarrow[\text{– SiMe}_4]{\text{H}_2 \text{ (75 atm), 25 °C, PhMe}}$

Ln = Y (**385**), Yb (**386**), Lu (**387**)

Ln = Y (**395**), Yb (**396**), Lu (**397**)

3 $(Tp^{Me2})Ln(CH_2SiMe_3)_2(THF)$

Ln = Y (**388**), Nd (**391**),
Sm (**392**), Yb (**389**), Lu (**390**)

$\xrightarrow[\text{– SiMe}_4]{\substack{\text{H}_2 \text{ (75 atm), 25 °C} \\ \text{Et}_2\text{O or PhMe}}}$

Ln = Y (**398**), Sm (**399**),
Yb (**400**), Lu (**401**)

Ln = Nd (**402**)

$\xrightarrow[\text{– SiMe}_4]{\text{H}_2 \text{ (75 atm), THF}}$ $[(Tp^{Me2})YH_2]_3(THF)_{2-3}$

396

3 $(Tp^{iPr2})Ln(CH_2SiMe_3)_2$

Ln = Y (**379**), Lu (**380**)

$\xrightarrow[\text{– SiMe}_4]{\text{H}_2 \text{ (75 atm), pentane, 25 °C, 18~27 h}}$

Ln = Y (**404**), Lu (**405**)

Scheme 55

$(Tp^{R,R'})Ln(CH_2SiMe_3)_2(THF)$

R = R' = Me:
Ln = Y (**376**), Lu (**378**);
R = *t*Bu, R' = Me:
Ln = Y (**382**), Lu (**384**)

$\xrightarrow[\text{– SiMe}_4]{2 \text{ HC}\equiv\text{CR''}}$

Ln = Y:
R'' = Ph (**406**), SiMe$_3$ (**407**), *t*Bu (**408**), Ad (**409**);
Ln = Lu:
R'' = Ph (**410**), SiMe$_3$ (**411**), *t*Bu (**412**)

R = R' = Me, n = 1, Solv = 2,2'-bipyridine, R'' = Trit*:
Ln = Y (**413**), Lu (**414**);
R = R' = Me, n = 1, Solv = THF, R'' = *t*Bu:
Ln = Lu (**415**);
R = *t*Bu, R' = Me, n = 0, R'' = *t*Bu:
Ln = Y (**416**), Lu (**417**)

Scheme 56

Scheme 57

Scheme 58

Bis(alkyl) yttrium complex [Y(κ^3-To^M)(CH$_2$SiMe$_3$)$_2$(THF)] (**424**) was obtained by the reaction of Y(CH$_2$SiMe$_3$)(THF)$_2$ with an equimolar amount of tris(4,4-dimethyl-2-oxazolinyl)phenyl borate To^M (Fig. 30) [157].

According to the XRD analysis, To^M, as well as tris(pyrazolyl)borate ligands, is coordinated to the metal ion in a κ^3-*N,N,N*-fashion. In the crystalline state, complex **424** is very stable at room temperature and does not undergo decomposition even in a week, but in solution this compound completely decomposes within a day. A THF molecule can be easily substituted upon treatment with Ph$_3$P=O to form bis(alkyl) complex [Y(κ^3-To^M)(CH$_2$SiMe$_3$)$_2$(Ph$_3$PO)] (**425**) [157].

The monoanionic ligands based on bis(pyrazolyl)methane containing functional groups at the methine carbon atom ("heteroscorpionates") can bind covalently to the metal ion. Thus, Mountfond *et al.* reported that five-coordinated complex [(Me$_2$pz)$_2$CHSi(Me)$_2$N*i*Pr]Sc(CH$_2$SiMe$_3$)$_2$ (**426**) (pz = pyrazole) can be obtained by the reaction of (Me$_2$pz)$_2$CHSi(Me)$_2$N(H)*i*Pr

with Sc(CH$_2$SiMe$_3$)$_3$(THF)$_2$. In the case of yttrium, six-coordinated complex [(Me$_2$pz)$_2$CHSi(Me)$_2$N*i*Pr]Y(CH$_2$SiMe$_3$)$_2$(THF) (**427**) was derived (Scheme 59) [158]. These bis(alkyl) derivatives are stable in solution in an inert atmosphere for several days. Treatment of compound **426** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in the presence of THF yielded cationic alkyl complex [{(Me$_2$pz)$_2$CHSi(Me)$_2$N*i*Pr}Sc(CH$_2$SiMe$_3$)(THF)]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**428**) [158].

Treatment of Y(CH$_2$SiMe$_3$)$_2$(THF)$_2$ with an amidine that contained a quinoline substituent led to the formation of bis(alkyl) yttrium complex [NC$_9$H$_6$-8-NC(*t*Bu)NC$_6$H$_3$*i*Pr$_2$-2,6]Y(CH$_2$SiMe$_3$)$_2$(THF) (**429**) (Fig. 31) in 47% yield [159]. Accoridng to the X-ray diffraction analysis of complex **429**, the nitrogen atom of the quinoline fragment is coordinated to the metal atom. Bis(alkyl) derivative **429** exhibits high stability: no evidence of decomposition was detected in C$_6$D$_6$ at room temperature during a week [159]. Bis(alkyl) complexes

Figure 30

Ln = Sc, n = 0 (**426**);
Ln = Y, n = 1 (**427**)

Scheme 59

429

430   **431**
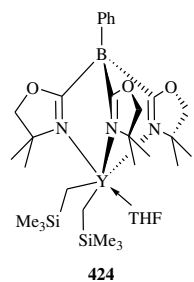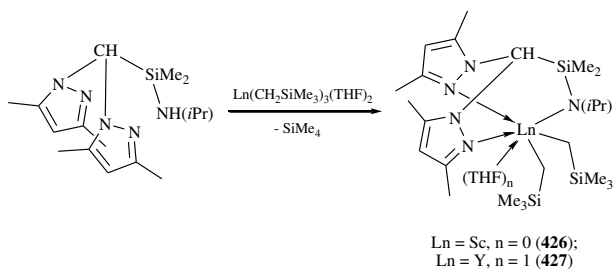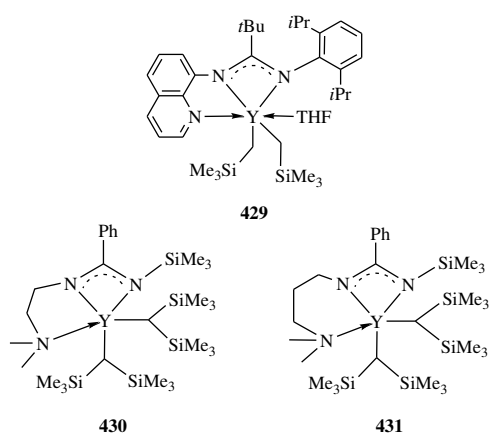
Figure 31

PhC(NSiMe₃)N(CH₂)ₙNMe₂]Y[CH(SiMe₃)₂]₂ (n = 2 (**430**), 3 (**431**)) were synthesized by the reactions of YCl₃(THF)₃.₅ with [PhC(NSiMe₃)N(CH₂)ₙNMe₂]Li (n = 2, 3) followed by the alkylation with two equivalents of LiCH(SiMe₃)₂ (Fig. 31) [63]. The XRD study of compound **430** showed that in this case the nitrogen atom of NMe₂ group was coordinated to the metal center.
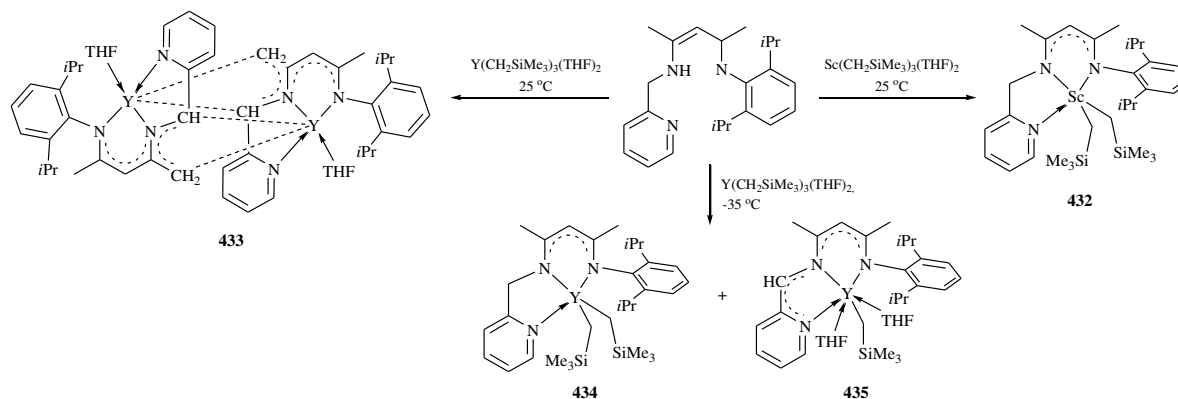
The interaction between tridentate β-diketimine ligand bearing a pendant pyridyl group (2,6-*i*Pr₂C₆H₃N=C(Me)CH=C(Me)-(NHCH₂C₅H₄N) with one equivalent of Sc(CH₂SiMe₃)₃(THF)₂ at room temperature afforded bis(alkyl) complex Sc(CH₂SiMe₃)₂ (**432**) in high yield (Scheme 60) [160]. In the case of Y(CH₂SiMe₃)₃(THF)₂, the reaction under similar conditions gave rise to dimeric complex **433**. In compound **433** the yttrium atom is coordinated by the new trianionic ligand, and no alkyl groups are retained. The formation of this ligand occurs as a result of the deprotonation of the methyl group in the β-diketiminate ligand and the methylene group attached to the pyridyl ring (Scheme 60) [160]. The same reaction performed at –35 °C afforded a mixture of bis(alkyl) (L₋H)Y(CH₂SiMe₃)₂ (**434**) and monoalkyl (L₋₂H)Y(CH₂SiMe₃)(THF)₂ (**435**) complexes (Scheme 60) [160]. A dianionic ligand (L₋₂H) in compound **435** is the product of deprotonation of the methylene group attached to the pyridyl ring. The coordination of the pyridyl fragment in complexes **432** and **435** was established by X-ray crystallography. Compound **434** decomposes at room temperature to form complex **435** [160].

N,N,N-tridentate β-diketimines [(2,6-*i*Pr₂C₆H₃N)C(Me)CHC(Me)(N(CH₂)₂NR₂)]⁻ (R = Me, Et; R−R = −(CH₂)₅) are excellent ligands for the synthesis and isolation of bis(alkyl) complexes of rare-earth elements, including metals with large ionic radii, such as neodymium and samarium. The interaction of freshly prepared tris(alkyl) derivatives Ln(CH₂SiMe₃)₃(THF)ₙ with equimolar amounts of β-diketimines led to the formation of five-coordinated bis(alkyl) lanthanide complexes [(2,6-*i*Pr₂C₆H₃N)C(Me)CHC(Me)(N(CH₂)₂NR₂)]Ln(CH₂SiMe₃)₂ (R = Me: Ln = Y (**436**), Lu (**437**), Sm (**438**), Nd (**439**); R = Et, Ln = Y (**440**); R−R = −(CH₂)₅, Ln = Y (**441**)) (Fig. 32) [161]. X-ray diffraction studies of the compounds revealed the coordination of one of side donor groups. This coordination is also retained in [(2,6-*i*Pr₂C₆H₃NH)C(Me)CHC(Me)(N(CH₂)₂N(Me)-(CH₂)₂NMe₂)]Sc(CH₂SiMe₃)₂ (**442**) was synthesized by the reaction of Sc(CH₂SiMe₃)₃(THF)₂ with (2,6-*i*Pr₂C₆H₃NH)C(Me)CHC(Me)(N(CH₂)₂N(Me)(CH₂)₂NMe₂) solution [161]. Bis(alkyl) scandium complex (Fig. 32) [162]. According to the data of X-ray diffraction analysis, the potentially tetradentate *N,N,N,N*-β-diketiminate ligand is coordinated to the scandium atom in a monoanionic tridentate fashion. No contact between NMe₂ group and the metal center was detected [162].

433   **432**

434   +   **435**

Scheme 60

R = Me: Ln = Y (**436**), Lu (**437**),
Sm (**438**), Nd (**439**);
R = Et: Ln = Y (**440**);
R-R = (CH₂)₅: Ln = Y (**441**)

442
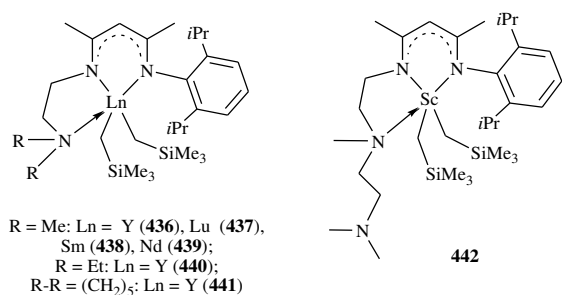
Figure 32

Chen *et al.* showed that bis(alkyl) scandium complex **442** can be used as a precursor for the synthesis of terminal amido derivative containing the double Sc=N bond [(2,6-*i*Pr₂C₆H₃NH)C(Me)CHC(Me)(N(CH₂)₂N(Me)-(CH₂)₂NMe₂)]Sc=NC₆H₃*i*Pr₂-2,6 (**444**). This complex was formed by the protonolysis of **442** with NH₂C₆H₃*i*Pr₂-2,6 followed by the thermal decomposition of alkyl-anilide compound **443** in hexane at 50 °C (Scheme 61) [163]. It is important to note that the conversion of the starting bis(alkyl) complex **442** and alkyl-anilide derivative **443** to compound **444** proceeds with a change in the type of ligand coordination. Thus, in complexes **442** and **443** the β-diketiminate ligand is bound to the scandium atom in a κ³-*N,N,N*-mode, while in complex **444** the ligand is tetradentate. The interaction between *in situ* generated dimethyl scandium complex [(2,6-*i*Pr₂C₆H₃N)C(Me)CHC(Me)(N(CH₂)₂NMe₂)]ScMe₂ (**445**) and NH₂C₆H₃*i*Pr₂-2,6 led to the formation of expected methyl-

anilide derivative [(2,6-*i*Pr₂C₆H₃N)C(Me)CHC(Me)(N(CH₂)₂NMe₂)]ScMe(NHC₆H₃*i*Pr₂-2,6) (**446**) (Scheme 61) [163]. No transformations were observed upon heating of complex **446** in C₆D₆ at 70 °C for two days. However, terminal imido complex [(2,6-*i*Pr₂C₆H₃N)C(Me)CHC(Me)(N(CH₂)₂NMe₂)]Sc=NC₆H₃*i*Pr₂-2,6(NC₅H₄NMe₂-4) (**447**) was obtained by the reaction with the Lewis base *N,N*-dimethylaminopyridine (DMAP) (Scheme 61) [163].

N,N,N-tridentate anilideimine ligand with 8-quinoline substituent was used for the synthesis of bis(alkyl) complexes of rare-earth elements (*o*-C₆H₄N-(C₉H₆N)CH=NC₆H₃*i*Pr₂-2,6)Ln(CH₂SiMe₃)₂(THF)ₙ (Ln = Sc, n = 0 (**448**); Ln = Y, n = 1 (**449**); Ln = Lu, n = 0 (**450**)) (Fig. 33) [164].

Treatment of a tridentate ligand having a seven-membered 6-imino-6-methyl-1,4-diazepine skeleton and imine substituent, PhCH=NCMe[(CH₂NMeCH₂)₂], with Y(CH₂SiMe₃)₃(THF)₂ led to the addition of one alkyl group across the C=N bond and the formation of the corresponding bis(alkyl) complex {PhCH(CH₂SiMe₃)NCMe-[(CH₂NMeCH₂)₂]}Y(CH₂SiMe₃)₂(THF) (**451**) (Scheme 62) [165].

Bis(alkyl) scandium complexes stabilized by monoanionic κ³-tridentate ligand {6-RNCMe[(CH₂NMeCH₂)₂]}-Sc(CH₂SiMe₃)₂(THF) (R = Me (**452**), SiMe₂Ph (**453**)) were synthesized by the reactions of Sc(CH₂SiMe₃)₃(THF)₂ with 6-RNH-1,4,6-trimethyl-1,4-diazepine (R = Me; R = SiMe₂Ph) (Scheme 63) [166].

Ar = C₆H₃*i*Pr₂-2,6

442 → **443** → **444**

445 → **446** → **447**

Scheme 61

Ln = Sc, n = 0 (**448**);
Ln = Y, n = 1 (**449**);
Ln = Lu, n = 0 (**450**)

Figure 33

451

Scheme 62

R = Me (**452**), SiMe$_2$Ph (**453**)

Scheme 63

Ln = Sc (**458**), Y (**459**), Lu (**460**)
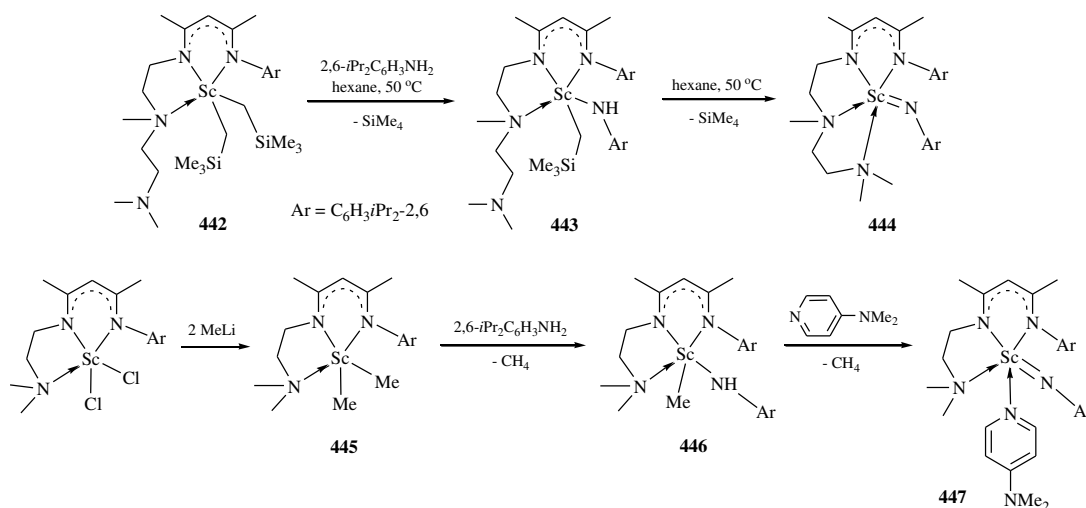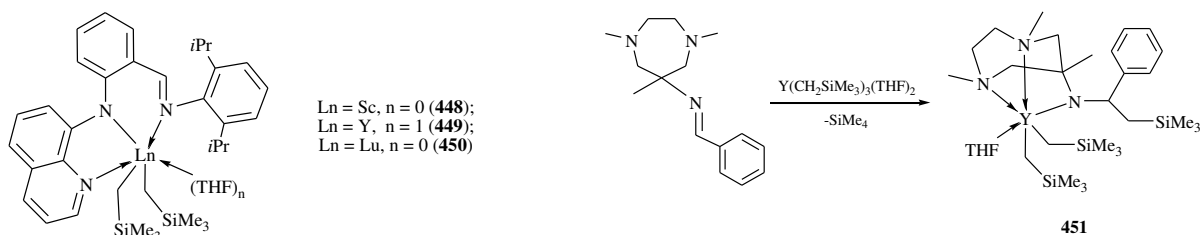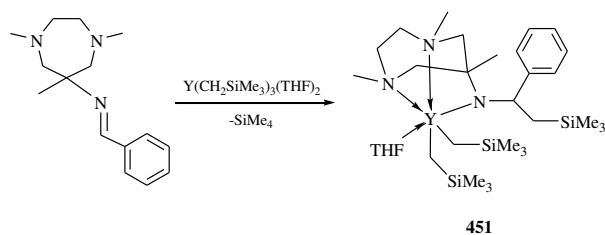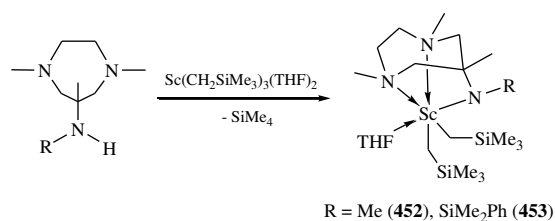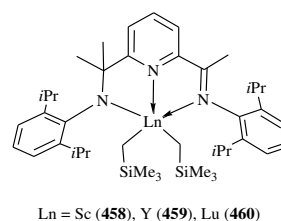
Figure 34
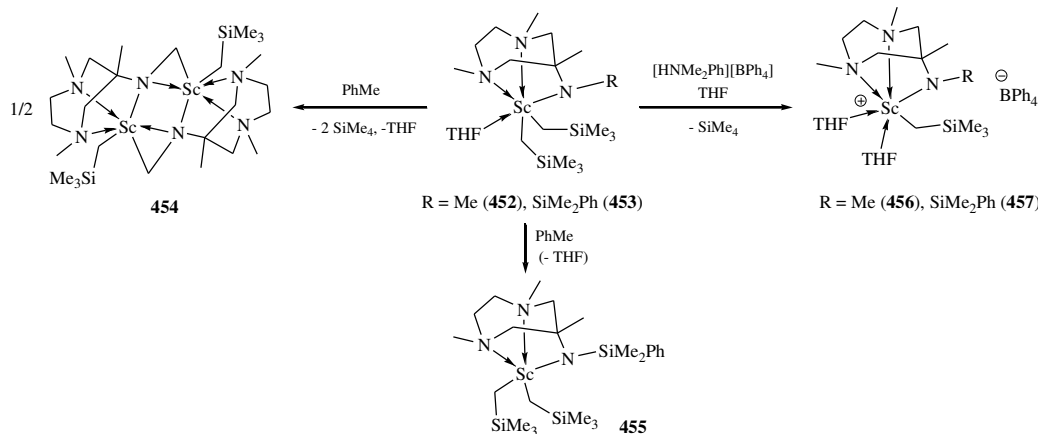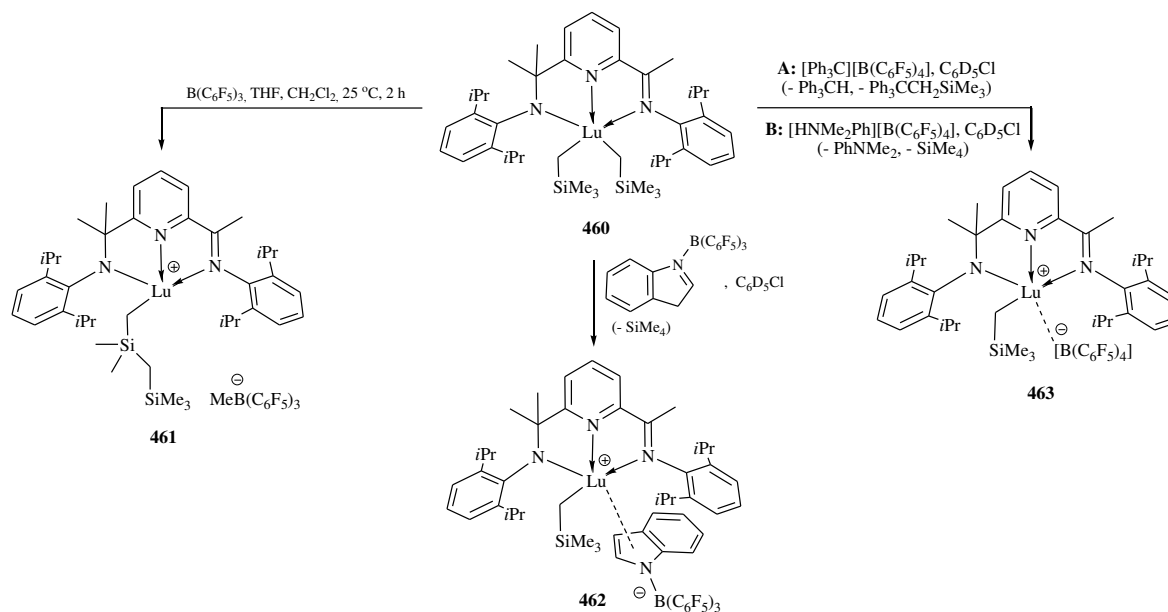
Scheme 64

Scheme 65

The stability and reactivity of these compounds strongly depend on the nature of the substituents at the amido group. In toluene at room temperature, the metal–THF coordination bond dissociates, and the metallation of the amide fragment results in {[CH$_2$(μ-N)-CMe[(CH$_2$NMeCH$_2$)$_2$]}Sc(CH$_2$SiMe$_3$)}$_2$ (**454**) and one equivalent of SiMe$_4$ (Scheme 64) [166]. In contrast, upon elimination of a THF molecule, scandium complex **453** gives stable THF-free bis(alkyl) derivative {6-PhMe$_2$SiNCMe[(CH$_2$NMeCH$_2$)$_2$]}Sc(CH$_2$SiMe$_3$)$_2$ (**455**) (Scheme 64) [166]. Cationic alkyl complexes [{6-RNCMe[(CH$_2$NMeCH$_2$)$_2$]}Sc(CH$_2$SiMe$_3$)(THF)$_2$][BPh$_4$] (R = Me (**456**), SiMe$_2$Ph (**457**)) were synthesized by the reactions of

bis(alkyl) complexes **452** and **453** with [HNMe$_2$Ph][BPh$_4$] (Scheme 64) [166].

A tridentate iminoamidopyridinate ligand was also used to synthesize bis(alkyl) complexes of rare-earth elements [167, 168]. Thus, the interaction between 2-{(2,6-*i*Pr$_2$C$_6$H$_3$)N=CMe}-6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NHCMe$_2$}C$_5$H$_3$N and Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) led to the formation of solvent-free complexes [2-{(2,6-*i*Pr$_2$C$_6$H$_3$)N=CMe}-6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}C$_5$H$_3$N]-Ln(CH$_2$SiMe$_3$)$_2$ (Ln= Sc (**458**) [168], Y (**459**) [168], Lu (**460**) [167]) (Fig. 34). The reaction was accompanied by the formation of SiMe$_4$ and the elimination of two THF molecules.

At room temperature, complexes **458–460** undergo slow decomposition with the formation of the free ligand and SiMe$_4$. The interaction between lutetium derivative **460** and B(C$_6$F$_5$)$_3$ in a CD$_2$Cl$_2$/THF mixture resulted in cationic alkyl complex [2-{(2,6-*i*Pr$_2$C$_6$H$_3$)N=CMe}-6-{(2,6-*i*Pr$_2$C$_6$H$_3$)NCMe$_2$}C$_5$H$_3$N]-Lu(CH$_2$SiMe$_2$CH$_2$SiMe$_3$)(THF)][MeB(C$_6$F$_5$)$_3$] (**461**) (Scheme 65) [167]. The reaction of **460** with *N*-[tris(pentafluorophenyl)borane]-3H-indole yielded compound **462** (Scheme 65) [168]. Cationic alkyl complex **463** was derived upon treatment of **460** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (Scheme 65) [168].

The reactions of Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with equimolar amounts of 2,2':6,2"-terpyridine or 4,4',4"-tritert-butyl-2,2':6,2"-terpyridine were accompanied by 1,3-migration of one alkyl group to the *ortho*-position of the central pyridine ring to form bis(alkyl) derivatives **464** and **465** in quantitative yields (Scheme 66) [169]. In these complexes, the lutetium atom is coordinated by the monoanionic ligands due to the loss of aromaticity of the heterocycle.

Polydentate amidineaminopyridines {HN^{Me2}NN^{Me2}C^{Me}N^{R2}} (R = Me, *i*Pr) were introduced in σ-bond metatheses with tris(alkyl) (Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$, Ln = Sc, Y) and tris(aminobenzyl) (Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$) derivatives of rare-earth elements (Fig. 35) [170, 171]. As a result, the following bis(alkyl) scandium and yttrium complexes coordinated by the *N,N,N*-tridentate ligands were obtained: {N^{Me2}NN^{Me2}C^{Me}N^{R2}}Ln(CH$_2$SiMe$_3$)$_2$(THF) (R = Me, Ln = Y (**466**) [170]; R = *i*Pr, Ln = Sc (**467**); R = *i*Pr, Ln = Y (**468**) [171]) and {N^{Me2}NN^{Me2}C^{Me}N^{Me2}}Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (**469**) [170].

Complex **466** is unstable at –30°C in toluene and undergoes selective intramolecular activation of the methyl group C(sp^3)–H bond in 2,6-Me-C$_6$H$_3$ substituent at the imine nitrogen atom, resulting in complex {N^{Me2}NN^{Me2}C^{Me}N^{Me}CH$_2$}YCH$_2$SiMe$_3$(THF) (**470**) (Scheme 67) [170]. Complexes **467** and **468** with diisopropylphenyl substituents at the imine nitrogen atom showed high thermal stability: no evidence of decomposition was observed upon heating in hydrocarbon solvents at 60 °C for several days [171].

Bis(alkyl) rare-earth complexes stabilized by *N,N,N*-pincer monoanionic bis(iminophenyl)amido {[2,6-*i*Pr$_2$C$_6$H$_3$N=CHC$_6$H$_4$]$_2$N}Ln(CH$_2$SiMe$_3$)$_2$ (**471–473**) [172] and bis(oxazolinylphenyl)amido [(4-RC$_3$NOC$_6$H$_4$)$_2$N]-Ln(CH$_2$SiMe$_2$R')$_2$ (**474–478**) [173, 174] ligands were synthesized by the alkane elimination from the corresponding tris(alkyl) compounds (Fig. 36).

It should be noted that bis(alkyl) complexes with CH$_2$SiMe$_3$ groups can be prepared only for the scandium and lutetium aatoms (compounds **474** and **475**, respectively). In the case of yttrium and thulium, dimeric monoalkyl compounds of a general formula [({4-*i*PrC$_3$NOC$_6$H$_4$}{OCH$_2$C(*i*Pr)N=C(CH$_2$SiMe$_3$)C$_6$H$_4$}N)-Ln(CH$_2$SiMe$_3$)]$_2$ (Ln = Y (**479**), Tm (**480**)) were formed (Scheme 68) [173]. According to the X-ray diffraction analysis, complexes **479** and **480** resulted from the migration of one trimethylsilylmethyl group from the metal atom to the oxazoline ring followed by the ring opening and the formation of the Ln–O bond.

Scheme 66

R = Me, Ln = Y (**466**);
R = *i*Pr: Ln = Sc (**467**), Y (**468**)

Figure 35

Scheme 67

R = *i*Pr, R' = Me: Ln = Sc (**474**), Lu (**475**);
R = *i*Pr, R' = Ph, Ln = Y (**476**);
R = Ph, R' = Ph, Ln = Y (**477**);
R = Bn, R' = Ph, Ln = Y (**478**)

Figure 36

Ln = Y (**479**), Tm (**480**)
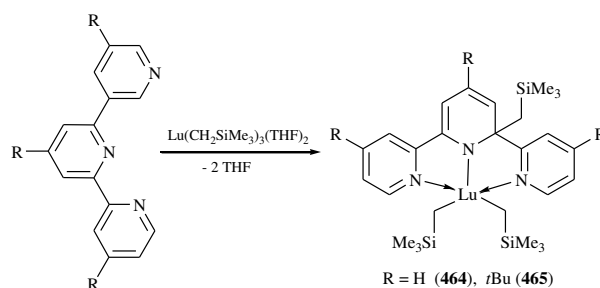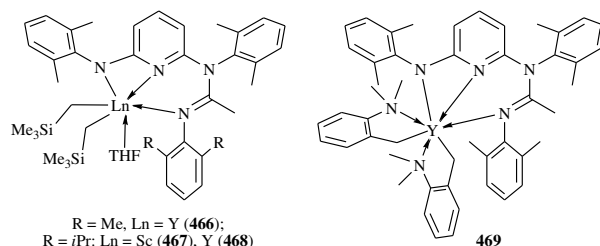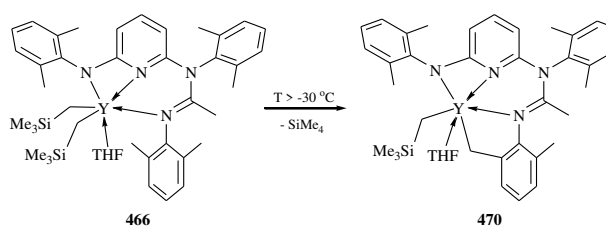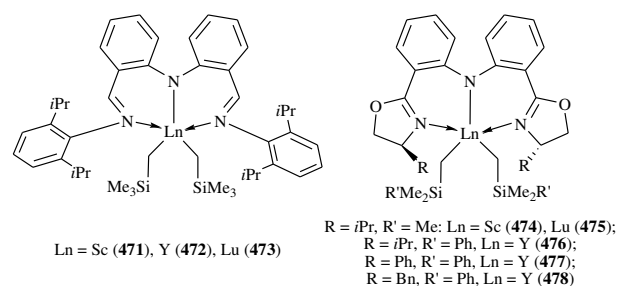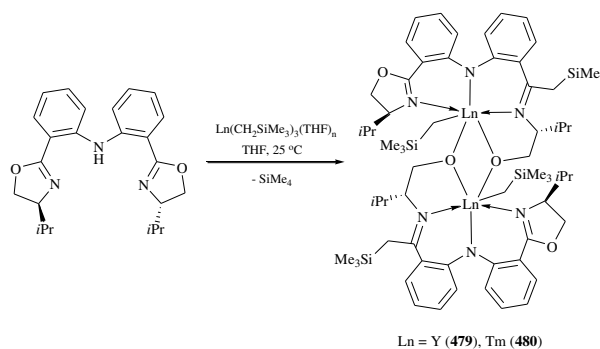
Scheme 68

Cui *et al.* demonstrated that pincer bis(aryl) phosphazene ligands $[N(PPh_2NAr)_2]^-$ (Ar = Ph, $C_6H_3Me_2$-2,6, $C_6H_3iPr_2$-2,6) are suitable coordination environments for the synthesis and isolation of bis(alkyl) complexes of rare-earth elements. The interaction of $HN(PPh_2NAr)_2$ with $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y, Lu) led to solvent-free complexes $[N(PPh_2NC_6H_3R_2$-2,6)_2]Ln(CH_2SiMe_3)_2$ (R = H: Ln = Sc (**481**), Y (**482**), Lu (**483**)); R = Me, Ln = Sc (**484**); R = *i*Pr: Ln = Y (**485**), Lu (**486**)) (Fig. 37) [175]. Complexes **481**–**486** feature κ^3-type coordination mode of the ligands.

Bis(alkyl) scandium derivative **481** was successfully employed for the synthesis of a terminal imide complex. Alkyl-anilide compound $[N(PPh_2NPh)_2]Sc(CH_2SiMe_3)(NHC_6H_3iPr_2$-2,6) (**487**) was obtained by the reaction of **481** with an equimolar amount of 2,6-$iPr_2C_6H_3NH_2$ in toluene at –30 °C. The subsequent treatment with 4-dimethylaminopyridine (DMAP) afforded imide complex $[N(PPh_2NPh)_2]Sc=NC_6H_3iPr_2$-2,6 (**488**) (Scheme 69) [176].

The reactions of pyrazolyl-substituted carbazoles 3,6-Me_2-1,8-$(C_3H_2N_2$-R-2)_2$-CarbH (R = Me, *i*Pr) with $Lu(CH_2SiMe_3)_3(THF)_2$ in toluene at room temperature resulted in the corresponding bis(alkyl) complexes [3,6-Me_2-1,8-$(C_3H_2N_2$-R-2)_2$-Carb]Lu(CH_2SiMe_3)_2 (R = Me (**489**), *i*Pr (**490**)) in high yields (Fig. 38) [177]. Complexes **489** and **490** demonstrated high thermal stability at room temperature both in solution and in the crystalline state. No signs of decomposition were observed upon heating of these compounds in C_6D_6 at 70 °C for 12 hours. Trinuclear hydride complex $\{[(CzPziPr)Lu]_2[(CzPziPr_{-H})Lu](\mu$-H)_5\}$ (**491**) was synthesized by the hydrogenation of **490** with H_2 (4 atm) in toluene at 50 °C (Fig. 39) [177]. XRD study showed that two lutetium atoms are coordinated by the monoanionic carbazole ligand, while the

third lutetium atom is bound to the dianionic ligand, which results from the intramolecular metallation of one pyrazole substituent. Three metal atoms are linked together by three μ^2-H and two μ^3-H hydride ligands.

Bis(alkyl) complexes of rare-earth elements $(CzxR)Ln(CH_2SiMe_3)_2$ (Ln = Y (**492**), Er (**493**), Yb (**494**)) stabilized by bis(oxazolyl)-substituted 1,8-bis(4',4'-dimethyloxazolin-2'-yl)-3,6-di-*tert*-butylcarbazole (CzxH) were obtained by the protonolysis of the corresponding tris(alkyl) derivatives (Scheme 70) [178]. Compounds **492**–**494** can also be synthesized by the alkylation of dichloride compounds $(Czx)LnCl_2(THF)$ with two equivalents of $LiCH_2SiMe_3$. Treatment of yttrium bis(alkyl) complex **492** with $[Ph_3C][B(C_6F_5)_4]$ afforded cationic alkyl compound $[(Czx)Y(CH_2SiMe_3)]^+[B(C_6F_5)_4]^-$ (**495**) [178].

Unlike pyrazolyl- and oxazolyl-substituted carbazoles, bis(phosphinimine)-functionalized carbazole ligands HCzPNAr are not suitable for synthesis and isolation of bis(alkyl) complexes of rare-earth elements. Lutetium bis(alkyl) derivatives $(CzPNAr)Lu(CH_2SiMe_3)_2$ (Ar = Ph (**496**), C_6H_4iPr-4 (**497**)) were prepared by the reactions of $Lu(CH_2SiMe_3)_3(THF)_2$ with HCzPNAr at –78 °C in C_7D_8. Complexes **496** and **497** are highly unstable and readily undergo double metallation of the C–H bonds at the *ortho*-position of the phenyl rings at the phosphorus atom, resulting in bis(aryl) compounds (Ar = Ph (**499**), C_6H_4iPr-4 (**500**)) (Scheme 71) [179]. The interaction between 3,6-Me_2-1,8-$(Ph_2P=NAr)_2$-carbazole (Ar = $C_6H_2Me_3$-2,4,6) with the mesityl substituent at the nitrogen atoms and $Y(CH_2SiMe_3)_3(THF)_2$ led to the formation of similar unstable bis(alkyl) derivative $(CzPNAr)Y(CH_2SiMe_3)_2$ (Ar = $C_6H_2Me_3$-2,4,6 (**498**)), which rapidly converted to cyclometallated yttrium complex (**501**) (Scheme 71) [180].

481   **487**   **488**

Scheme 69

R = H: Ln = Sc (**481**), Y (**482**), Lu (**483**);
R = Me: Ln = Sc (**484**);
R = *i*Pr: Ln = Y (**485**), Lu (**486**)

Figure 37

R = Me (**489**), *i*Pr (**490**)

Figure 38

491
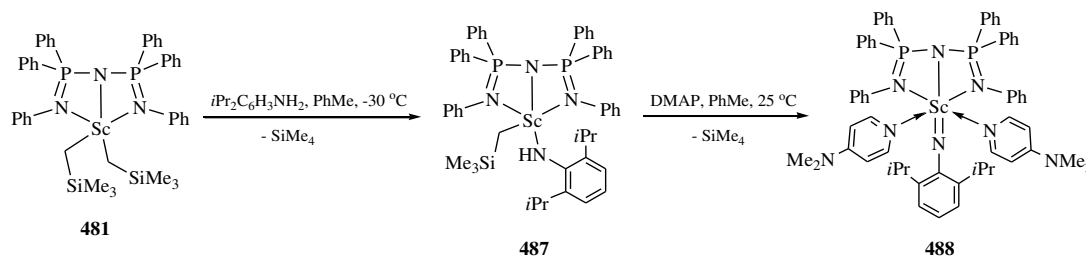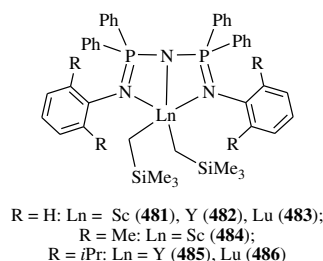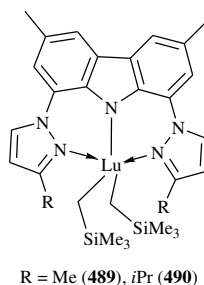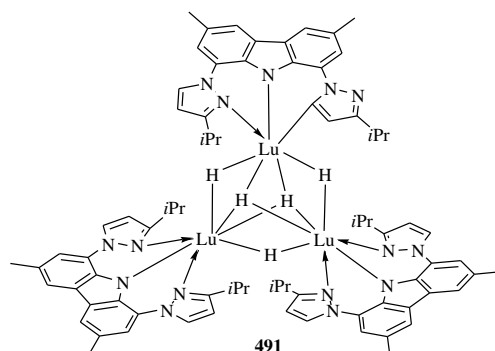
Figure 39
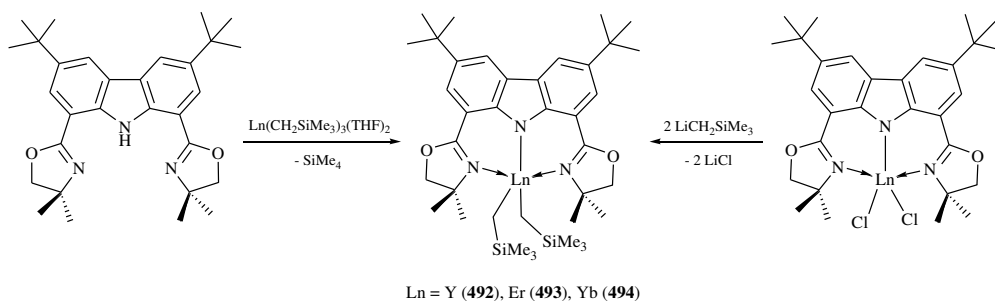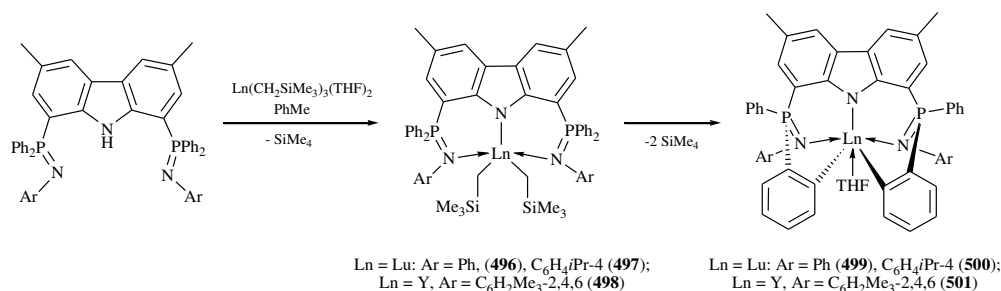
Scheme 70

Scheme 71
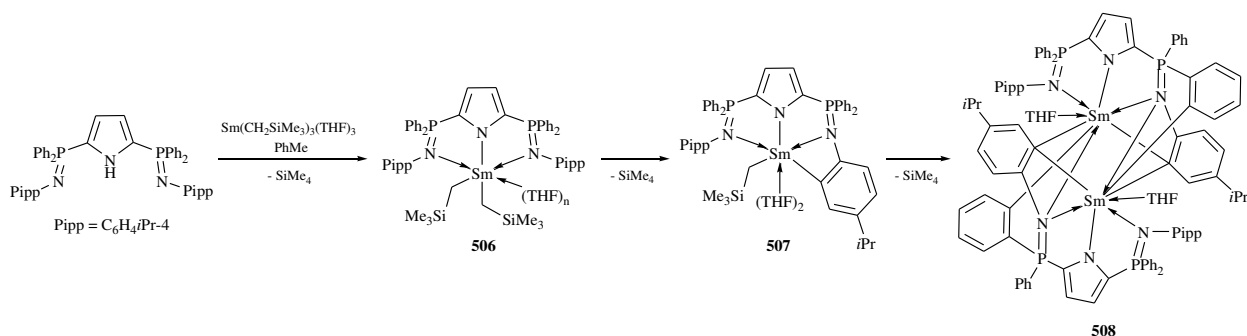
Scheme 72

The use of bis(phosphinimine)pyrrole allowed one to avoid side processes of *ortho*-metallation. Solvent-free bis(alkyl) complexes [2,5-(Ph$_2$P=NC$_6$H$_4$*i*Pr-4)$_2$C$_4$H$_2$N]Ln(CH$_2$SiMe$_3$)$_2$ (Ln = Sc (**502**), Er (**503**), Lu (**504**) [181], Y (**505**) [182]) were synthesized by the reactions of Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Er, Lu, Y) with 2,5-(Ph$_2$P=NC$_6$H$_4$*i*Pr-4)$_2$C$_4$H$_2$NH in high yields (Fig. 40).

Lutetium complex **504** demonstrated high stability in solution. No traces of decomposition were observed even upon heating at 60 °C for 4.5 h. An attempt to synthesize a similar compound of rare-earth element with the larger ionic radius (Sm^{3+}) afforded cyclometalled adduct **507** (Scheme 72) [182]. The authors noted that bis(alkyl) complex **506** is extremely unstable and rapidly undergoes cyclometallation at one of the aryl substituents on the nitrogen atom to form four-membered azamacrocycle κ^4-[2,5-(Ph$_2$P=NC$_6$H$_3$*i*Pr-4)$_2$C$_4$H$_2$N]Sm(CH$_2$SiMe$_3$)(THF)$_2$ (**507**). Monoalkyl derivative **507** is stable at low temperature in the solid state, but in solution it slowly undergoes the intramolecular C–H bond activation followed by the dimerization which results in complex [κ^1:κ^2:μ^2-LBSm(THF)]$_2$ (**508**) [182].

Treatment of complex **504** with one equivalent of oxonic acid [H(OEt$_2$)$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ yielded cationic alkyl derivative

{[2,5-(Ph$_2$P=NC$_6$H$_4$*i*Pr-4)$_2$C$_4$H$_2$N]Lu(CH$_2$SiMe$_3$)(OEt$_2$)$_2$}$^+$ {B(C$_6$F$_5$)$_4$}$^-$ (**509**) [181]. Alkyl-anilide complex [2,5-(Ph$_2$P=NC$_6$H$_4$*i*Pr-4)$_2$C$_4$H$_2$N]Lu(CH$_2$SiMe$_3$)(NHC$_6$H$_2$*t*Bu$_3$-2,4,6)(DMAP) (**510**) was obtained by the reaction of **504** with 2,4,6-*t*Bu$_3$C$_6$H$_2$NH$_2$ in the presence of DMAP at 100 °C [181].

The reactions of *N,N,N*-tridentate 2,5-bis((pyrrolidine-1-yl)methylene)-1H-pyrrole and 2,5-bis((piperidine)methylene)-1H-pyrrole with Ln(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (Ln = Sc, Y, Lu) led to bis(alkyl) complexes [2,5-(C$_4$H$_8$NCH$_2$)$_2$C$_4$H$_2$N]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_n$ (Ln = Sc, n = 0 (**511**); Ln = Y, n = 1 (**512**); Ln = Lu, n = 1 (**513**)) and [2,5-(C$_5$H$_{10}$NCH$_2$)$_2$C$_4$H$_2$N]Sc(CH$_2$SiMe$_3$)$_2$ (**514**) in moderate and good yields (Fig. 41) [183]. Unlike the complexes of yttrium

Ln = Sc (**502**), Er (**503**), Lu (**504**), Y(**505**)

Figure 40

Ln = Sc, n = 0 (**511**),
Ln = Y, n = 1 (**512**),
Ln = Lu, n = 1 (**513**)

514
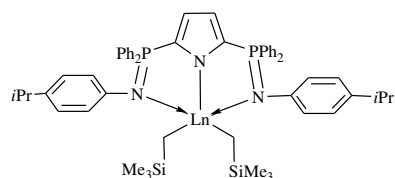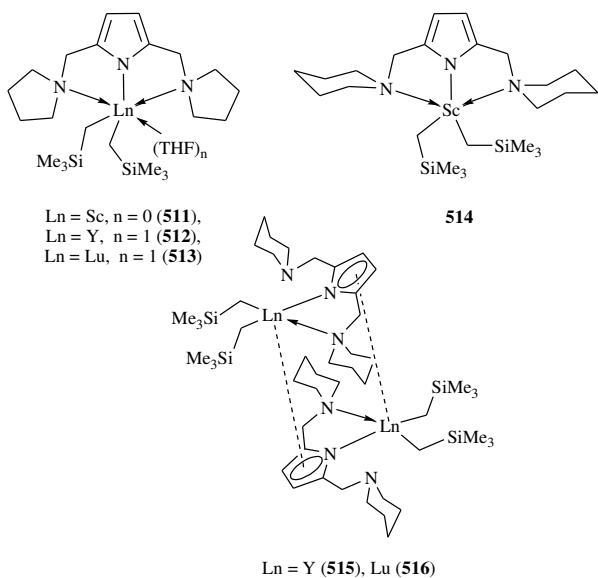
Ln = Y (**515**), Lu (**516**)

Figure 41

and lutetium (**512** and **513**), bis(alkyl) derivative of scandium **511** does not contain a coordinated THF molecule. Dimeric tetra(alkyl) complexes [2,5-$(C_5H_{10}NCH_2)_2C_4H_2N]_2Ln_2(CH_2SiMe_3)_4$ (Ln = Y (**515**), Lu (**516**)) (Fig. 41) were also synthesized. In complexes **515** and **516** two metal atoms are bound by the anionic pyrrole fragments featuring $\eta^5{:}\eta^5/\kappa^1{:}\kappa^1$-coordination mode [183].

3.4. Rare-earth bis(alkyl) complexes with the tetradentate *N*-containing ligands

The synthesis of bis(alkyl) complexes of rare-earth elements was also accomplished using 12-membered *N,N,N,N*-macrocyclic amine, namely, 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane. Treatment of (Me_3TACD)H with an equimolar amount of Ln(CH_2SiMe_3)_3(THF)_2 led to the corresponding bis(alkyl) derivatives (Me_3TACD)Ln(CH_2SiMe_3)_2 (Ln = Sc (**517**) [184], Y (**518**), Ho (**519**), Lu (**520**) [185]) in moderate and good yields (Scheme 73).

Trinuclear hexahydride clusters $[(Me_3TACD)Ln(\mu^2\text{-}H)_2]_3$ (Ln = Y (**521**), Ho (**522**), Lu (**523**)) were synthesized by the reactions of (Me_3TACD)Ln(CH_2SiMe_3)_2 **518**–**520** with PhSiH_3 (Fig. 42) [185].

Hessen *et al.* reported the synthesis of a series of bis(alkyl) rare-earth complexes **524**–**538** containing 9-membered macrocyclic triazacyclononanes (TACN) with various substituents at the nitrogen atoms (Fig. 43) [186–189].

Solvent-free bis(alkyl) complexes $[R^1_2TACN(CH_2)_2NR^2]Y(CH_2SiMe_3)_2$ (**524** [186], **527**, **528** [189], **530** [186]) and $[R^1_2TACNSiMe_2NR^2]Y(CH_2SiMe_3)_2$ (**533**, **534** [189], **537** [188]) were obtained by the reactions of Y(CH_2SiMe_3)_3(THF)_2 with disubstituted triazacyclononananamines R^1_2TACN-(B)-NHR^2 having dimethylene (B = (CH_2)_2, R^1 = Me, R^2 = *t*Bu, *sec*Bu, *n*Bu; R^1 = *i*Pr, R^2 = *t*Bu) or dimethylsilyl (B = SiMe_2, R^1 = Me, R^2 = *t*Bu, *sec*Bu; R^1 = *i*Pr, R^2 = *t*Bu) linkers between the macrocyclic fragment and the amine group (Fig. 43). The related scandium

complexes [Me_2TACNSiMe_2NR]Sc(CH_2SiMe_3)_2 (R = *t*Bu (**532**), *sec*Bu (**535**)) were also reported (Fig. 43) [189]. The interaction between Y(CH_2SiMe_3)_3(THF)_2 and Me_2TACN(CH_2)_2NH*t*Bu in pentane led to the formation of hardly soluble binuclear complex $\{[\eta^3{:}\eta^1\text{-}$Me_2TACN(CH_2)_2NtBu]Y(CH_2SiMe_3)\}\{\eta^3{:}\mu\text{-}\eta^1\text{-}$[Me_2TACN(CH_2)_2NtBu]Y(CH_2SiMe_3)_3\} (**539**) (Scheme 74) [189]. According to the XRD analysis data, one of the TACN-amido ligands is coordinated to one metal center through three nitrogen atoms, while the amido group is covalently bound to the other metal atom. In order to exclude the formation of this adduct, the reaction of the tris(alkyl) yttrium complex with triazacyclononanamine was carried out in THF.

In addition it should be noted that the ligand systems based on triazacyclononane are perfectly suitable for the stabilization of bis(alkyl) derivatives of rare-earth elements with large ionic radii. Treatment of *in situ* generated [La(CH_2SiMe_3)_3] with R^1_2TACN-(B)-NH*t*Bu at room temperature in THF resulted in bis(alkyl) complexes $[R^1_2TACN$-(B)-N*t*Bu]La(CH_2SiMe_3)_2 (B = (CH_2)_2, R^1 = Me (**525**) [187], R^1 = *i*Pr (**531**) [188]; B = SiMe_2, R^1 = *i*Pr (**538**) [188]) (Fig. 43). In the case of 4,7-dimethyl substituted ligand Me_2TACNSiMe_2NH*t*Bu, the bis(alkyl) complex underwent rapid metallation of the NMe group to form

(Me_3TACD)H

[Ln(CH_2SiMe_3)_3(THF)_2]
C_6D_6, 25 °C, 18 h
or
pentane, -20 °C
− SiMe_4

Ln = Sc (**517**), Y (**518**),
Ho (**519**), Lu (**520**)

Scheme 73

Ln = Y (**521**), Ho (**522**), Lu (**523**)

Figure 42

R^1 = Me, R^2 = *t*Bu: Ln = Y (**524**), La (**525**), Nd (**526**);
R^1 = Me, R^2 = *sec*Bu, Ln = Y (**527**);
R^1 = Me, R^2 = *n*Bu: Ln = Y (**528**), Nd (**529**);
R^1 = *i*Pr, R^2 = *t*Bu: Ln = Y (**530**), La (**531**)

R^1 = Me, R^2 = *t*Bu: Ln = Sc (**532**), Y (**533**), Nd (**534**);
R^1 = Me, R^2 = *sec*Bu: Ln = Sc (**535**), Y(**536**);
R^1 = *i*Pr, R^2 = *t*Bu: Ln = Y (**537**), La (**538**)
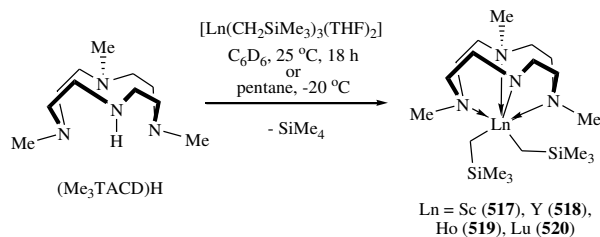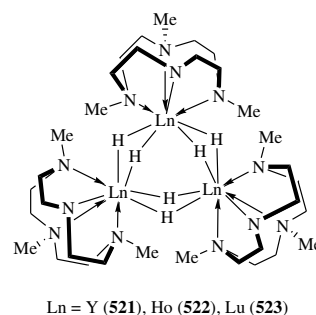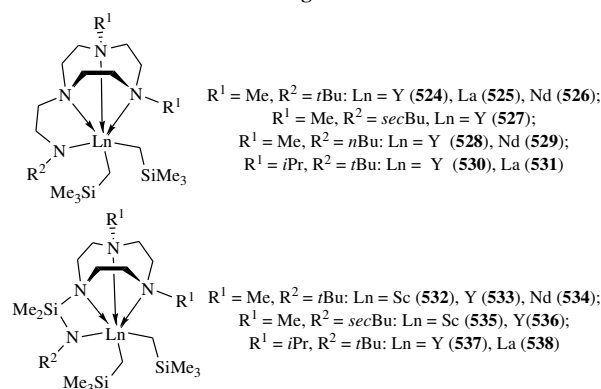
Figure 43

Scheme 74

Figure 44

R = SiMe₃, Ln = Y (**543**);
R = Ph: Ln = Sc (**544**), Y (**545**), La (**546**)
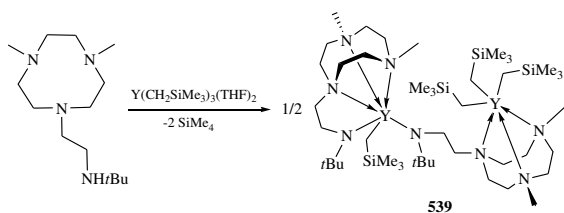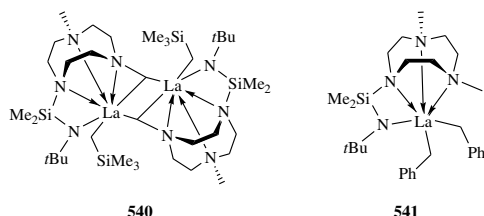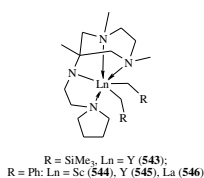
Figure 45

binuclear compound {[Me(μ-CH₂)TACN-(SiMe₂)N*t*Bu]La(CH₂SiMe₃)}₂ (**540**) [188]. In contrast, lanthanum dibenzyl complex [Me₂TACNSiMe₂N*t*Bu]La(CH₂Ph)₂ (**541**) was isolated from the reaction of La(CH₂Ph)₃(THF)₃ and Me₂TACNSiMe₂NH*t*Bu in 65% yield (Fig. 44) [188].

Bis(alkyl) neodymium complexes [Me₂TACN(B)NR²]Nd(CH₂SiMe₃)₂ (B = (CH₂)₂, R² = *t*Bu (**526**), *n*Bu (**529**); B = SiMe₂, R² = *t*Bu (**534**)) (Fig. 43) were synthesized by the reactions of NdCl₃(THF)₃ with three equivalents of Me₃SiCH₂Li followed by the treatment with Me₂TACN-(B)-NHR² in THF at room temperature [189]. Ccomplexes [*i*Pr₂TACN-(B)-N*t*Bu]Ln(CH₂SiMe₃)₂ **530**, **531**, **537**, and **538** slowly decompose in C₆D₆ at room temperature. Compound **531** is the least stable complex with a half-life of 30 min at 35 °C. Its decomposition is accompanied by the elimination of an equivalent of SiMe₄ and propene. In the case of bis(alkyl) derivatives [Me₂TACN-(B)-NR²]Ln(CH₂SiMe₃)₂ **526–529**, **532–536** (B = (CH₂)₂, SiMe₂; R² = *t*Bu, *sec*Bu, *n*Bu; Ln = Sc, Y, Nd) (Fig. 43), no signs of decomposition were observed in solution at room temperature during one day [189].
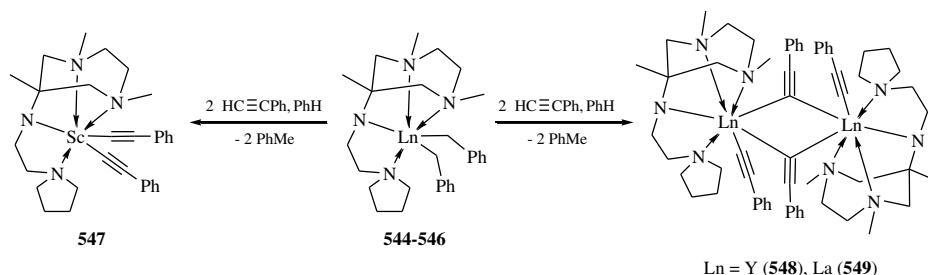
The reaction of complex **525** with two equivalents of phenylacetylene yielded binuclear bis(alkynyl) complex [Me₂TACN(CH₂)₂N*t*Bu]La(C≡CPh)(μ-C≡CPh)}₂ (**542**) [187]. Cationic alkyl complexes {[R¹₂TACN-(B)-NR²]Ln(CH₂SiMe₃)(THF)ₙ}⁺{BAr₄}⁻ were obtained upon treatment of bis(alkyl) yttrium (**524**, **527**, **528**, **530**, and **533**) and lanthanum (**525**, **531**, and **538**) complexes with the Brönsted acids ([HNMe₂Ph][B(C₆F₅)₄], [HNMe₂Ph][BPh₄], and [Ph₃C][B(C₆F₅)₄]) [184–187].

Monoanionic tridentate ligand 1,4,6-trimethyl-*N*-(2-pyrrolidine-1-yl-ethyl)-1,4-diazepane-6-amine (LH) with a seven-membered ring was used for the synthesis of bis(alkyl) complexes of rare-earth elements [190]. Solvent-free compounds (**L**)Ln(CH₂R)₂ (R = SiMe₃, Ln = Y (**543**) [190]; R = Ph, Ln = Sc (**544**), Y (**545**), La (**546**) [191]) resulted from the alkane elimination during the reaction between LH and Ln(CH₂R)₃(THF)ₙ (R = SiMe₃, Ph; Ln = Sc, Y, La) in toluene or THF (Fig. 45).

Compounds **544–546** are very thermally stable and can be stored in solution or in the solid state without decomposition for several months. In contrast, yttrium complex **543** bearing CH₂SiMe₃ alkyl groups gradually decomposes in C₆D₆ at room temperature with the release of SiMe₄. In all the compounds explored, the azepine fragment of the ligand is coordinated to the metal center. Complexes **543–546** can be converted to the corresponding cationic derivatives [(**L**)Ln(CH₂R)]⁺[B(C₆F₅)₄]⁻ by the reactions with [HNMe₂Ph][B(C₆F₅)₄] in C₆D₅Br. The treatment of **544** with two equivalents of phenylacetylene resulted in monomeric bis(alkynyl) complex (**L**)Sc(C≡CPh)₂ (**547**), while yttrium (**545**) and lanthanum (**546**) compounds afforded dimeric products [(**L**)Ln(C≡CPh)(μ-C≡CPh)]₂ (Ln = Y (**548**), La (**549**)) (Scheme 75) [191].

Bambirra *et al.* [192] synthesized bis(alkyl) yttrium complexes [(Me₂NCH₂CH₂)₂N-(B)-N*t*Bu)]Y(CH₂SiMe₃)₂ (B = (CH₂)₂, SiMe₂) containing monoanionic tetradentate triaminoimide ligands. Complex [(Me₂NCH₂CH₂)₂N(CH₂)₂N*t*Bu]Y(CH₂SiMe₃)₂ (**550**) (Scheme 76) was isolated in 68% yield. The structure of **550** was confirmed by X-ray crystallography. Compound **550** is unstable at room temperature. Its decomposition is accompanied by the metallation of the methyl group of the NMe₂ fragment and leads to the formation of [{(CH₂)MeN(CH₂)₂}{Me₂N(CH₂)₂}N(CH₂)₂N*t*Bu]Y(CH₂SiMe₃) (**551**) (Scheme 76) [192]. In the case of the triamine-amido ligand containing Me₂Si-linker, the metallation proceeds very rapidly, resulting in [{(CH₂)MeN(CH₂)₂}{Me₂N(CH₂)₂}NSiMe₂N*t*Bu]Y(CH₂SiMe₃) (**552**) (Scheme 76) [192].

Ln = Y (**548**), La (**549**)
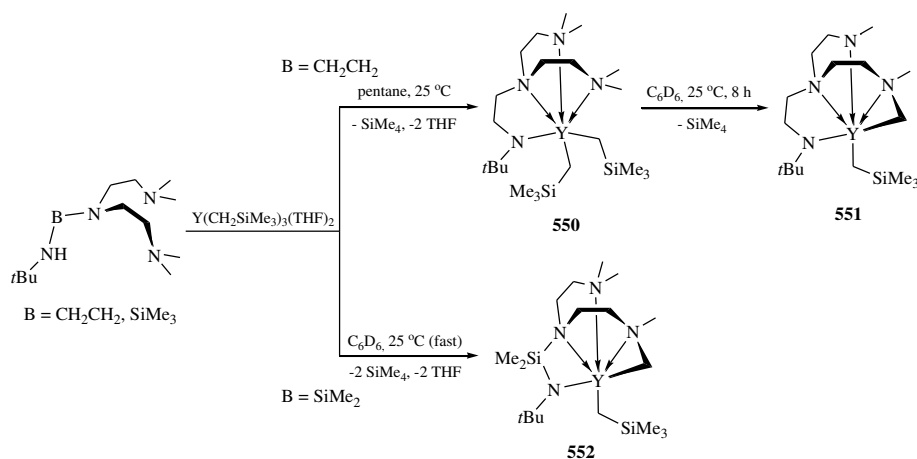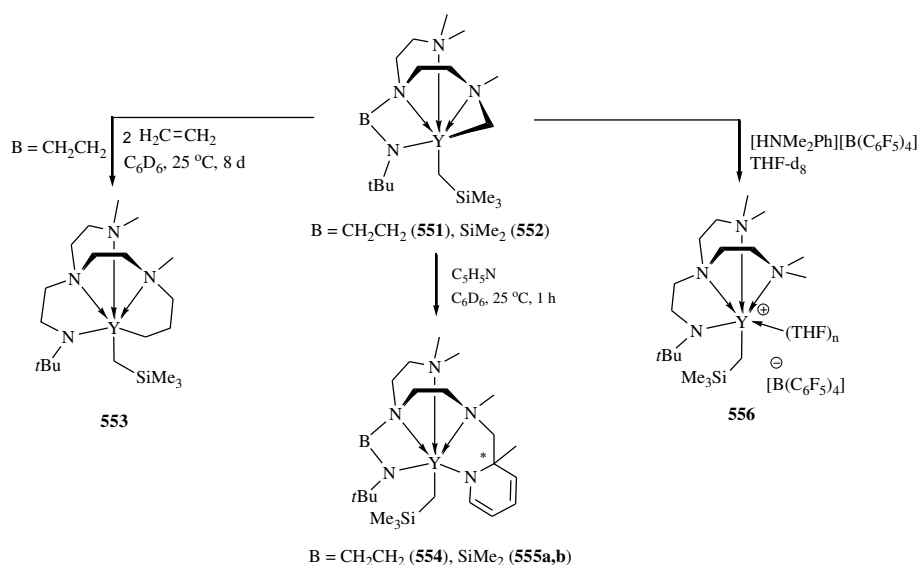
Scheme 75

Scheme 76

Scheme 77

Two Y–C bonds, YCH$_2$SiMe$_3$ and YCH$_2$N, in complex **551** demonstrated different reactivities. Thus, compound **551** underwent CH$_2$=CH$_2$ insertion and reacted with C$_5$H$_5$N and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] only *via* YCH$_2$N fragment, while the YCH$_2$SiMe$_3$ bond remained inactive. Complex **551** reacted very slowly with a stoichiometric amount of ethylene, which inserted into the YCH$_2$N bond to afford [{(CH$_2$)$_3$MeN(CH$_2$)$_2$}{Me$_2$N(CH$_2$)$_2$}N(CH$_2$)$_2$NtBu]-Y(CH$_2$SiMe$_3$) (**553**) (Scheme 77) [192]. Treatment of **551** with pyridine led to the rapid 1,2-addition across the YCH$_2$N bond to form [{(NC$_5$H$_5$CH$_2$)MeN(CH$_2$)$_2$}-{Me$_2$N(CH$_2$)$_2$}N(CH$_2$)$_2$NtBu]Y(CH$_2$SiMe$_3$) (**554**) (Scheme 77) [192]. The reaction of metallated product **552** with pyridine afforded a mixture of two diastereomeres [{(NC$_5$H$_5$CH$_2$)MeN(CH$_2$)$_2$}{Me$_2$N(CH$_2$)$_2$}-N(CH$_2$)$_2$NtBu]Y(CH$_2$SiMe$_3$) (**555a,b**) (Scheme 77) in 1:1 ratio [192]. Cationic alkyl complex [{(Me$_2$NCH$_2$CH$_2$)$_2$N(CH$_2$)$_2$NtBu)}Y(CH$_2$SiMe$_3$)(THF)$_n$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (**556**) (Scheme 77) was obtained by the reaction of **551** with the Brönsted acid [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] in deuterated THF [192].

Tetradentate β-diketiminate *N,N,N,N*-([MeC(NC$_6$H$_3$$i$Pr-2,6)CHC(Me)N(CH$_2$)$_2$N(Me)(CH$_2$)$_2NMe_2$],

[HC{CMe(N(CH$_2$)$_2$NEt$_2$}$_2$}]) ligands containing additional donor groups at one or both of the nitrogen atoms of the β-diketiminate fragment were used to synthesize bis(alkyl) complexes of yttrium and terbium [MeC(NC$_6$H$_3$$i$Pr-2,6)CHC(Me)N(CH$_2$)$_2$N(Me)(CH$_2$)$_2NMe_2$]YMe$_2$ (**557**) [193], [HC{CMe(N(CH$_2$)$_2$NEt$_2$}$_2$]Tb(CH$_2$SiMe$_3$)$_2$ (**558**) (Fig. 46). Compounds **557** and **558** were obtained by the reactions of the corresponding dichloride or dibromide derivatives with alkyllithium reagents (MeLi and LiCH$_2$SiMe$_3$) [193, 194]. According to the results of X-ray diffraction analyses, the atoms of rare-earth elements in complexes **557** and **558** have pseudo-octahedral coordination environments with the tetradentate β-diketiminate ligands in the equatorial planes. Two alkyl groups are located above and below these planes.
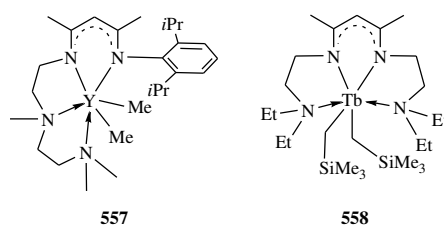
Figure 46

4. Conclusions

The data summarized in the present review clearly demonstrate that nitrogen-containing ligand systems of variable denticity are suitable coordination environments for organo-rare-earth metal species. The application of *N*-donor ligands provides stabilization of highly reactive rare-earth alkyl, bis(alkyl), cationic alkyl, and hydrido complexes. Owing to the high energy of the rare-earth–nitrogen bond, *N*-containing organic molecules are excellent frameworks for creating mono- and dianionic ligand systems that tightly bind the metal center. The availability of a variety of synthetic methods for the design of ligand systems and modification of their denticity ensures fine-tuning of the geometry of the central rare-earth metal ion, which, in turn, is an important task for homogeneous catalysis. The high catalytic potential of alkyl and bis(alkyl) complexes of rare-earth elements attract increasing interest of many research groups.

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