Russian Chemical Reviews **76** (11) 1051 – 1072 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n11ABEH003693

Non-metallocene rare-earth organometallic derivatives: synthesis, structure and application in the catalysis of transformations of unsaturated substrates †

A A Trifonov

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Abstract. The review summarises advances in the post-metallocene chemistry of rare-earth organometallic compounds. The synthesis, structures and reactivities of complexes containing metal – carbon and metal – hydrogen bonds and stabilised by N-, P- or O-donor ligands are considered. The catalytic activities of these compounds in alkene polymerisation, hydroamination, hydrosilylation and hydroboration are discussed. The bibliography includes 139 references.

I. Introduction

Organic derivatives of rare-earth metals (rare-earth elements, REE) have a unique combination of properties and are of considerable interest as catalysts for different reactions. Due to large ionic radii of rare-earth elements [1, 2] combined with Lewis acidity and the presence of unoccupied 5d and 6s orbitals (for Ln^{3+} ions), these compounds have a pronounced tendency to form complexes and exhibit high coordination numbers.[3] An insignificant contribution of the covalent component to rare-earth metal – ligand interactions removes restrictions associated with the compatibility of the orbitals in symmetry. This can give rise to radically new types of compounds the reactivity of which differs from that of d element derivatives. Due to the similarity of the redox and chemical properties of rare-earth elements combined with a substantial variation in the ionic radii in the series of these compounds (from 0.885 Å for Sc to 1.172 Å for La),[2] there is a unique possibility for optimising the reactivity of metal complexes by constructing the metal coordination sphere and choosing the appropriate radius of the central atom in accordance with specific features of the catalysed reaction. The fact that metallocene-type rare-earth metal alkyl and hydride complexes are efficient catalysts (or their precursors) for hydrogenation,[4–7] polymerisation,[8–10] hydrosilylation,[11] hydroboration,[12, 13] hydroamination [14–16] and hydrophosphination [17–19] of alkenes clearly demonstrates that these compounds have a high catalytic potential.

A A Trifonov G A Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, ul. Tropinina 49, 603950 Nizhnii Novgorod, Russian Federation. Fax (7-831) 462 74 97, tel. (7-831) 462 66 52, e-mail: trif@iomc.ras.ru

Received 9 January 2007
Uspekhi Khimii **76** (11) 1122 – 1144 (2007); translated by T N Safonova

Since rare-earth metals are electropositive and the metal – ligand interactions in their organic derivatives are predominantly ionic in character, ligands capable of forming stable anions were traditionally used in this field of chemistry. This is why cyclopentadienyl complexes have prevailed among known organic derivatives of REE until recent years.[20] The stability and reactivity of rare-earth organometallic compounds are largely determined by the degree of steric saturation of their coordination spheres with the result that certain requirement are imposed on the ligands. The latter should be rather bulky and fill the metal coordination sphere at low coordination numbers of metal atoms, resulting in the kinetic stability of metal complexes. The synthesis of complexes soluble in non-polar non-coordinating solvents is an important problem, the solution of which would allow the synthesis of derivatives containing no coordinated Lewis bases and bearing the central atoms with low coordination numbers. This would lead to an increase in the catalytic activity of complexes as a result of the exclusion of the competition between the Lewis base and the substrate for a site in the metal coordination sphere.

In recent years, the trend has been toward the design of new non-cyclopentadienyl ligand systems allowing for stabilisation of rare-earth metal alkyl ‡ and hydride complexes.[21–23] The aims of the replacement of ligands are to enhance stability of REE derivatives with retention of high catalytic activity, to increase the catalyst tolerance to functional groups of monomers, to extend the scope of the design and control of the geometry of the metal coordination sphere in complexes and to control the catalytic activity of metal complexes and the selectivity of the reactions. At the same time, studies of the influence of the coordination environment of rare-earth metal atoms on the reactivities of M – C and M – H bonds and the catalytic activity of compounds are of considerable interest. A comparison of the catalytic activities of rare-earth metal complexes containing anionic non-carbocyclic-type ligands with those of metallocene-type analogues would allow the determination of the relationship between the properties of metal complexes (structure, effective positive charges on metal

† Dedicated to Academician G A Abakumov on the occasion of his 70th birthday.

‡ Hereinafter, the term alkyl complexes is used in reference to complexes containing alkyl or substituted alkyl ligands (for example, CH_2SiMe_3, *etc*.).

atoms and Lewis acidity) and their activity in the catalysis of transformations of alkenes.

The present review summarises methods for the synthesis, structures, reactivities and catalytic activities of rare-earth metal complexes (alkyl, cationic alkyl, hydride, *etc*.) stabilised by N-, O- or P-donor ligands.

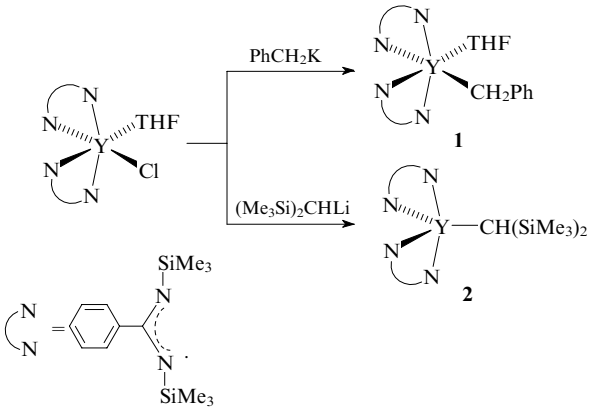
II. Neutral alkyl and aryl complexes

1. Monoalkyl and -aryl complexes

a. Complexes with monoanionic N-containing ligands

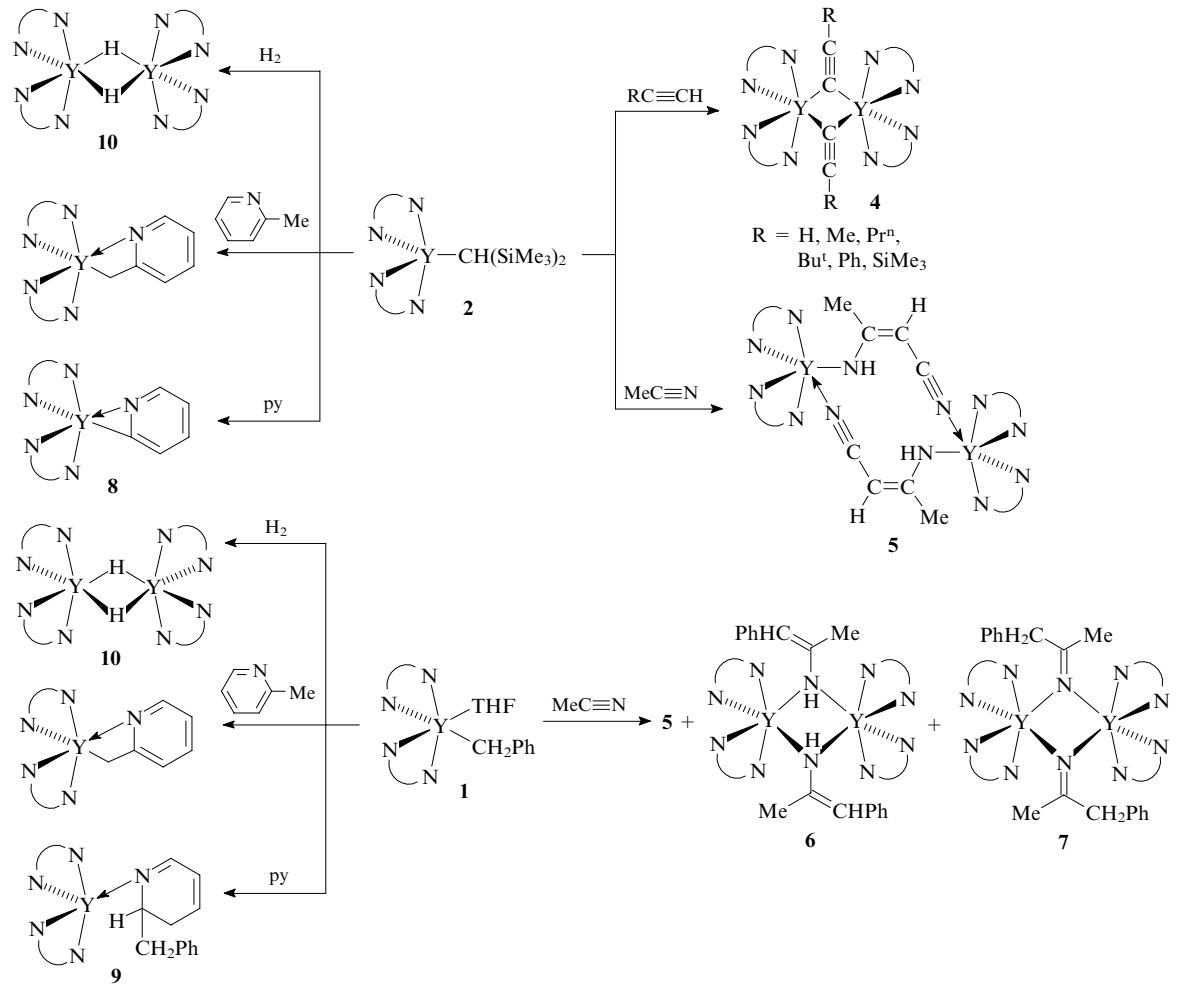
The bidentate amidinate anions $[R^1C(NR^2)_2]^-$ are among the first non-cyclopentadienyl ligands, which have been successfully used for stabilisation of rare-earth metal alkyl complexes. The monomeric yttrium derivatives $L_2YR(THF)$ [L = $PhC(NSiMe_3)_2$, R = CH_2Ph (**1**)] and L_2YR [L = PhC.$(NSiMe_3)_2$, R = $CH(SiMe_3)_2$ (**2**), L = *p*-$MeOC_6H_4C$.$(NSiMe_3)_2$; R = $CH(SiMe_3)_2$ (**3**)] were synthesised.[24]

Complexes **1**–**3** are thermally stable in deuteriocyclohexane or deuteriobenzene. No evidence of the H/D exchange, metallation of the solvent or thermal decomposition of the complexes was observed upon heating of these solutions at 100 °C for several hours. The X-ray diffraction study of complex **3** showed that this complex is monomeric. The steric parameters of the amidinate fragments are similar to those of the pentamethylcyclopentadienyl ligands, whereas their electronic properties are substantially different. Based on semi-empirical INDO/1 calculations for the model $[HC(NH)_2]_2YMe$ and $(\eta^5\text{-Cp})_2YMe$ complexes, it was concluded that the higher electron-withdrawing ability of amidinate ligands results in an increase in the positive charge on the yttrium atom in bis(amidinate) derivatives compared to metallocene-type analogues. The charge separation for the Y–C bond in the $[HC(NH)_2]_2YMe$ and $(\eta^5\text{-Cp})_2YMe$ complexes is 1.06 and 0.75 e, respectively, *i.e*., the bond in the former compound is much more polar. In the authors' opinion, the larger positive charge on the yttrium atom in $[HC(NH)_2]_2YMe$ leads to a larger orbital contraction, thus hindering interactions between the metal and the substrate (for example, H_2) and resulting in the absence of the H/D exchange and in lower hydrogenolysis rates compared to cyclopentadienyl derivatives.[24]



Compound **2** reacts with terminal alkynes to form dimeric acetylenide complexes **4** and activates C–H bonds in acetonitrile to give dimeric complex **5** (Scheme 1). The reaction of

Scheme 1

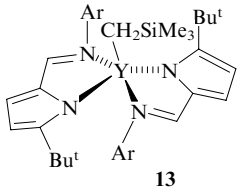


complex **1** affords, in addition to C–H bond activation product **5**, compounds **6** and **7** as a result of the insertion at the nitrogen–carbon double bond. The reaction of compound **2** with pyridine involves the metallation of the pyridine ring at the α position with respect to the nitrogen atom to give complex **8**. The reaction of compound **1** affords the addition product at the double bond of the heterocycle (compound **9**). The hydrogenolysis of compounds **1** and **2** gives rise to dimeric hydride **10** (see Scheme 1).[25,26]

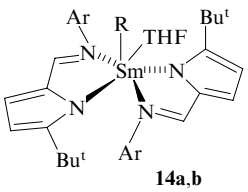
Alkyl and aryl derivatives of scandium stabilised by amidinate ions {$[PhC(NSiMe_3)_2]_2ScR$, R = CH_2SiMe_3 (**11**), Mes; $[PhC(NSiMe_3)_2]_2ScMe(THF)$} were synthesised by the exchange reaction of the chloride complex $[PhC(NSiMe_3)_2]_2$. .ScCl(THF) with the corresponding alkyllithium reagents.[27] The reactions of complex **11** with $Me_3SiC{\equiv}CH$ and H_2 produce monomeric acetylenide $[PhC(NSiMe_3)_2]_2Sc(C{\equiv}CSi$. $.Me_3)$ and dimeric hydride $[\{PhC(NSiMe_3)_2\}_2Sc(\mu\text{-}H)]_2$ (**11a**), respectively.

The tetrasubstituted guanidinate ligands $[R_2NC(NR')_2]^-$, like the amidinate anions, are N,N-chelating singly charged ligands and are of interest because of the simplicity of their synthesis, the diversity of coordination abilities and the ease of modifications of their electronic and steric characteristics.[28] Monomeric alkyl derivatives of yttrium with diisopropyl-substituted guanidinate ligands $[(Me_3Si)_2NC(NPr^i)_2]_2YR$ [R = Bu^t or $CH(SiMe_3)_2$] were synthesised and structurally characterised.[29] These compounds contain no coordinated Lewis bases, resulting in low coordination numbers of the central atom. Bulkier dicyclohexyl-substituted guanidinate ligands were also successfully used for the synthesis of alkyl and aryl derivatives of yttrium and samarium, *viz.*, L_2YBu^t (**12**), $L_2YPh(THF)$[30] and $L_2SmCH(SiMe_3)_2$[31] [L = $(Me_3Si)_2NC(NCy)_2$, Cy is cyclohexyl]. It should be noted that the yttrium atom in complex **12** is coordinatively saturated, resulting in the agostic interaction between the metal atom and two methyl groups of the *tert*-butyl substituent, which is responsible for short Y–C contacts and substantial deviations of the bond angles at the central carbon atom of the Bu^t group from the tetrahedral value.[30] X-Ray diffraction and ^{13}C NMR spectroscopic studies showed that agostic interactions exist not only in the crystalline state, but also in deuterobenzene.

Monoanionic bidentate pyrrolecarbaldiminate ligands (L) were successfully used in the synthesis of yttrium (**13**) and samarium (**14a**,**b**) complexes by the reactions of chlorides $L_2LnCl(THF)$ (Ln = Y or Sm) with the corresponding alkyllithium reagents in toluene.[32] Attempts to synthesise the methyl derivative of yttrium according to an analogous procedure failed. The monomeric structure of complex **14a** and the bidentate coordination of the ligands L were confirmed by X-ray diffraction.



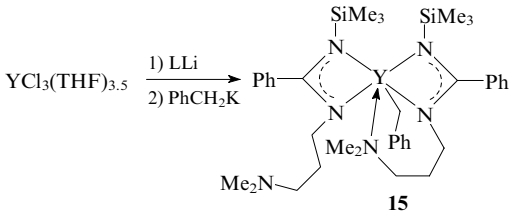
13



14a,**b**

Ar = 2,6-$Pr^i_2C_6H_3$; R = CH_2SiMe_3 (**a**), Me (**b**).

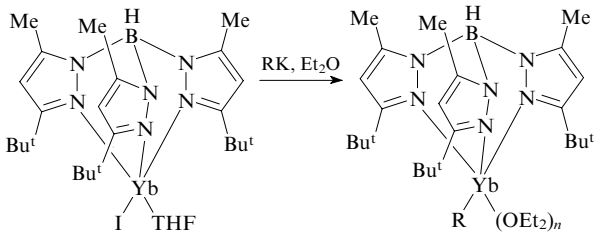
A tridentate amidinate ligand containing an additional donor group in the side chain was used for the synthesis of the corresponding benzyl derivatives of yttrium **15**.[33] The X-ray diffraction study showed that in the crystalline state, only one of the amino groups of the amidinate ligands is coordinated to the metal atom.



15

L = $PhC(NSiMe_3)N(CH_2)_3NMe_2$.

The monoanionic tridentate hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate ligand (TPB-Me,Bu^t) belongs to a few ligand systems allowing the synthesis of organometallic derivatives of divalent ytterbium (**16a**,**b**).



16a,**b**

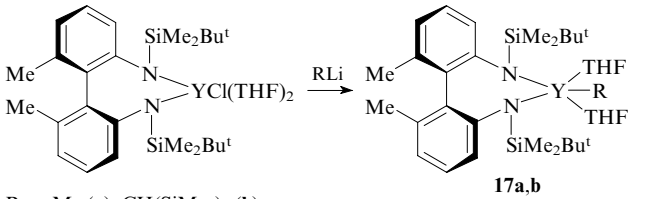
R = CH_2SiMe_3, *n* = 1 (**a**); R = $CH(SiMe_3)_2$, *n* = 0 (**b**).

Complex **16b** was studied by X-ray diffraction, which confirmed its monomeric structure. This compound readily reacts with phenylacetylene to form the corresponding acetylenide $LYb(C{\equiv}CPh)$.[34]

Complexes with dianionic N-containing ligands

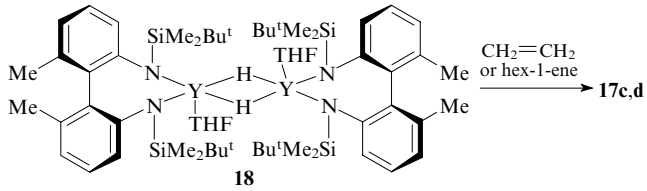
Diamide ligands, which differ in the number of donor groups, as well as in the nature and length of the bridge between the functional groups, are among the most widely used ligands in chemistry of rare-earth non-cyclopentadienyl ligands. The sterically rigid dianionic ligand 2,2′-bis(*tert*-butyldimethylsilylamido)-6,6′-dimethylbiphenyl (DADMB) was used for the synthesis of alkyl derivatives of yttrium. The coordination of this ligand to the metal atom gives rise to the seven-membered metallacycle. Compounds **17a**,**b** were synthesised by the exchange reactions of the starting chloride (DADMB)YCl(THF)$_2$ with MeLi and $(Me_3Si)_2CHLi$, respectively (Scheme 2). Analogous ethyl and n-hexyl complexes **17c**,**d** were prepared by the addition of hydride **18** at the double bonds of ethylene and hex-1-ene, respectively, in THF.[35] The structure of compound **17c** was established by X-ray diffrac-

Scheme 2



17a,**b**

R = Me (**a**), $CH(SiMe_3)_2$ (**b**).

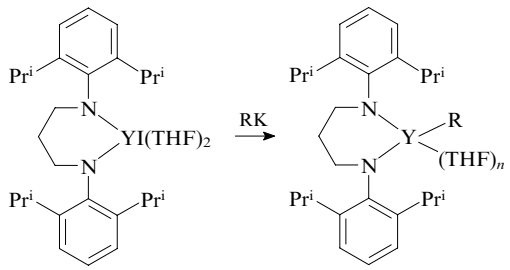


18

R = Et (**c**), n-C_6H_{13} (**d**).

tion. This study demonstrated that complex **17c** is monomeric, and the yttrium atom is additionally coordinated by two THF molecules.

The use of a sterically less rigid ligand (L), in which two amide groups are linked by the propylene bridge, allowed the synthesis of more strained six-membered metallacyclic derivatives of yttrium. The reactions of iodo derivative **19** with $PhCH_2K$ and $(Me_3Si)_2CHK$ afforded complexes **20a**,**b**; their structures were established by X-ray diffraction.[36,37] Both complexes proved to be rather stable in deuterobenzene at room temperature and are inert to hex-1-ene and ethylene.

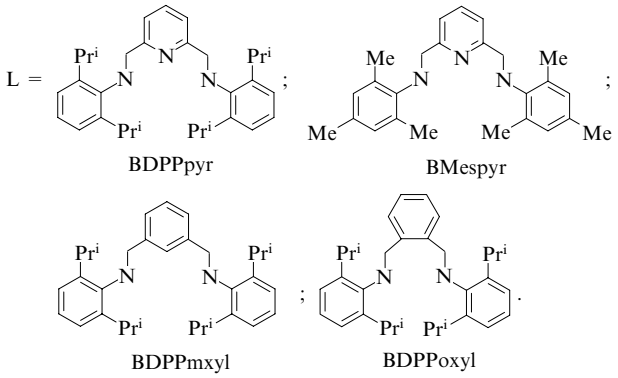


19 **20a**,**b**

R = CH_2Ph, n = 2 (**a**); R = $CH(SiMe_3)_2$, n = 1 (**b**).

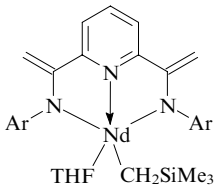
Diamino-substituted pyridines and benzenes (LH_2), which can act as bi- and tridentante ligands, were used for the synthesis of scandium, yttrium and lutetium derivatives by the elimination of tetramethylsilane from the tris(trimethylsilylmethyl) derivatives $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y or Lu) in the reactions with LH_2.

$$LH_2 + Ln(CH_2SiMe_3)_3(THF)_2 \xrightarrow[-2\ SiMe_4]{} LLnCH_2SiMe_3(THF)_n,$$

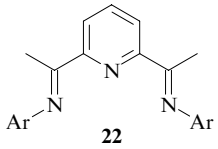


The monomeric complexes $(BDPPpyr)LnCH_2SiMe_3.(THF)_n$ (n = 1, Ln = Sc or Lu; n = 2, Ln = Y) proved to be rather stable at room temperature in hexane; their stability was found to decrease with increasing ionic radius of the metal atom. Derivatives of the sterically less hindered pyridine-containing analogue BMespyr, for example, $(BMespyr).LnCH_2SiMe_3(THF)_n$ (n = 1, Ln = Sc; n = 2, Ln = Lu), appeared to be less stable under analogous conditions (hexane, 20 °C), the yttrium compound being unstable to an extent that attempts to isolate this compound at room temperature failed. Alkyl derivatives $(BDPPoxyl)LnCH_2SiMe_3(THF)$ (Ln = Sc, Lu or Y) were synthesised in good yields with the use of diamino-substituted benzene BDPPoxyl, which, unlike pyridine-containing ligands, cannot be intramolecularly stabilised by the coordination of the nitrogen atom to metal but which contains the bulky isopropyl substituents in the aniline fragments.[38]

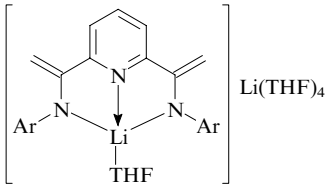
An unusual approach to the synthesis of trimethylsilylmethyl derivative of neodymium **21** containing the tridentate 2,6-diiminopyridine ligand was proposed.[39] The partial alkylation of the starting $NdCl_3(THF)_3$ with RLi (R = CH_2SiMe_3) is followed by the reaction with diimine **22** or lithium salt **23** depending on the Nd : R ratio (1 : 4 or 1 : 2, respectively). The dianion is formed as a result of C—H bond activation in the methyl groups at the imine carbon atoms of the 2,6-diiminopyridine fragment of 2,6-$(2,6\text{-}Pr^i_2C_6H_3N{=}CMe)_2C_5H_3N$. The structure of complex **21** was established by X-ray diffraction.



21



Ar = $2,6\text{-}Pr^i_2C_6H_3$.

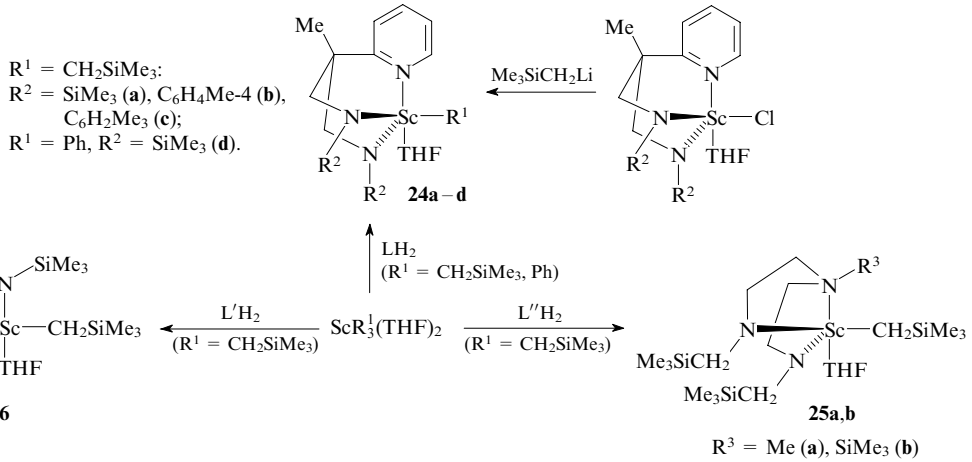


23

Ar = $2,6\text{-}Pr^i_2C_6H_3$.

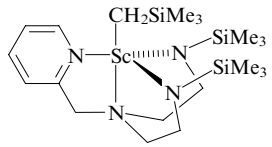
Diamido-pyridine- and diamido-amine-type tridentate dianionic ligands (LH_2) have also found use in recent years. For example, five-coordinate scandium alkyl and aryl complexes **24a**–**d**, **25a**,**b**, **26** (Scheme 3) and **27** were synthesised starting

Scheme 3



26

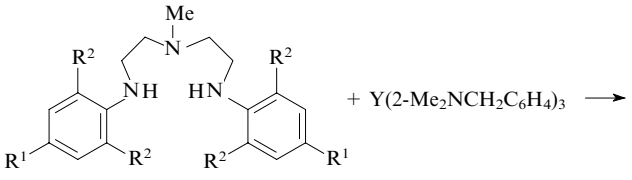
from anhydrous chloride $ScCl_3$ by two successive exchange reactions or by the protolysis of the corresponding $R_3Sc(THF)_2$ derivatives (R = CH_2SiMe_3 or Ph) with an equimolar amount of a neutral ligand.[40–42].

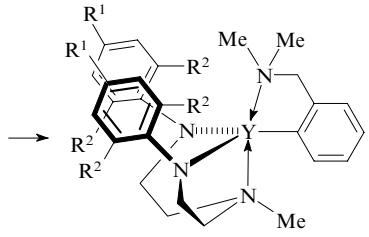


27

The X-ray diffraction study showed that five-coordinate compounds **24c** and **27** are monomeric, whereas the four-coordinate complex [{(MeC(2-C_5H_4N)($CH_2NC_6H_4$Me-4)$_2$}.$ScCH_2SiMe_3]_2$, which contains no coordinated THF molecules, has (in the crystalline state) the dimeric structure due to the presence of two bridging amide groups.

Yttrium complexes **28a–c** with σ-bonded aryl ligands containing an additional donor group were synthesised[43] by the elimination of arene in the reactions of the corresponding amines with the triaryl derivative. Compound **28a** decomposes at 25 °C, whereas complexes **28b**,**c** are much more stable.

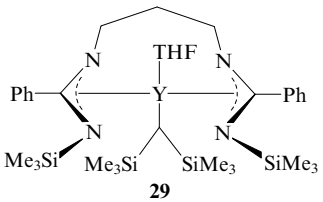




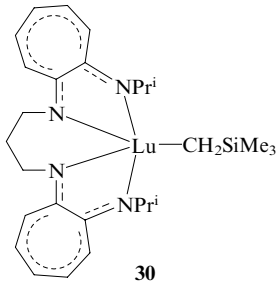
28a–c

R^1 = R^2 = Me (**a**); R^1 = H: R^2 = Et (**b**), Cl (**c**).

Alkyl complexes with tetradentate dianionic ligands are represented by bis(amidinate) (**29**)[44] and aminotropone iminate (**30**)[45] derivatives.



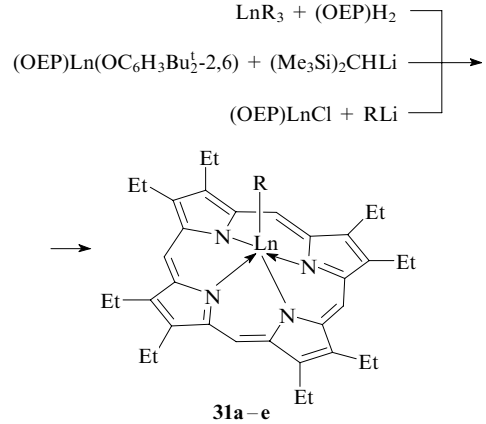
29



30

c. Complexes with dianionic N-containing macrocyclic ligands

Rare-earth metal complexes with macrocyclic ligands have attracted attention due mainly to their luminescence and magnetic properties.[46] However, examples of the use of N-containing macrocyclic ligands as the stabilising coordination environment for alkyl derivatives of rare-earth elements are scarce. The doubly deprotonated octaethylporphyrin (OEP) macrocycle was successfully used for the synthesis of alkyl derivatives of yttrium (**31a**), lutetium (**31b**)[47] and scandium (**31c–e**).[48] Complexes **31a**,**b** were synthesised in 70%–80% yields by the reactions of octaethylporphyrin $(OEP)H_2$ with the $Ln[CH(SiMe_3)_2]_3$ derivatives (Ln = Y or Lu) involving elimination of alkane and by the exchange reactions of the corresponding phenoxides $(OEP)Ln(OC_6H_3Bu^t_2$-2,6) (Ln = Y or Lu) with $(Me_3Si)_2CHLi$. The resulting compounds proved to be thermally rather stable and withstand heating in toluene at 60 °C for 6 h. The structure of complex **31b** was established by X-ray diffraction. The coordination sphere of the lutetium atom can be described as a square pyramid formed by the coordinated slightly curved OEP ligand and the $CH(SiMe_3)_2$ group. Scandium compounds **31c–e** were prepared by the reactions of chloride (OEP)ScCl with the corresponding alkyllithium reagents. According to the X-ray diffraction study, complexes **31c**,**d** are structurally similar to lutetium complex **31b**.

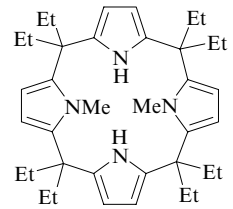


31a–e

Ln = Y, R = $CH(SiMe_3)_2$ (**a**); Ln = Lu, R = $CH(SiMe_3)_2$ (**b**);
Ln = Sc: R = Me (**c**), CH_2SiMe_3 (**d**), $CH(SiMe_3)_2$ (**e**).

Derivatives **31a**,**b** readily react with $HOC_6H_3Bu^t_2$-2,6, $Bu^tC{\equiv}CH$ and H_2O to give monomeric phenoxide $(OEP)Ln(OC_6H_3Bu^t_2$-2,6), dimeric acetylenide [(OEP)Ln.$(\mu$-$C{\equiv}CBu^t)]_2$ and dimeric hydroxide $[(OEP)Ln(\mu$-$OH)]_2$, respectively. Unlike compounds **2** and **17a**,**b**, complexes **31a**,**b** do not react with hydrogen even under a pressure of 25 atm (25 °C).[47] Scandium derivatives **31c–e** readily bind at the C=O double bond of carbon monoxide and at the C=N double bond of xylyl isocyanate; however, the reactions afford inseparable mixtures of products. The reactions of methyl derivative **31c** with CO_2 and acetone also readily proceed at room temperature to give, respectively, the acetate and *tert*-butoxide complexes.[48]

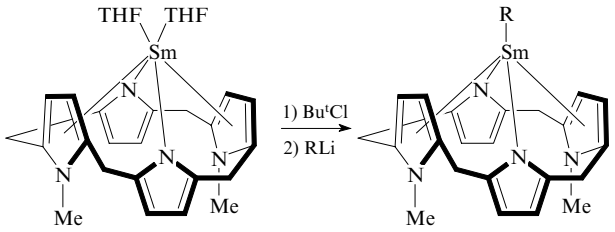
trans-*N*,*N*-Dimethylated porphyrinogen (PORF) was used as a convenient polydentate ligand, which allowed the synthesis of monomeric alkyl complexes of trivalent samarium **32a**,**b** containing no coordinated solvent molecules, halide ions or alkali metals.[49]



$(PORF)H_2$

The divalent samarium derivative $(PORF)Sm(THF)_2$ was used as the starting compound. The oxidation of this compound with *tert*-butyl chloride followed by the treatment with the corresponding derivative RLi afforded complexes **32a**,**b**,

their structures were confirmed by X-ray diffraction (the ethyl groups are omitted for simplicity).



32a,**b**

R = Me (**a**), CH_2SiMe_3 (**b**)

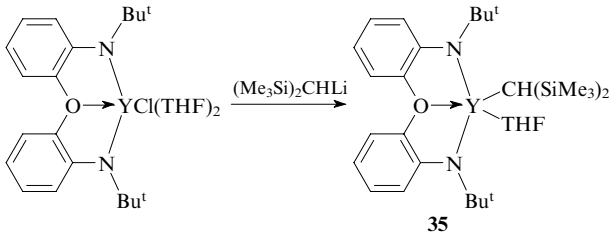
Unlike metallocene-type samarium methyl complexes, complex **32a** appeared to be rather inert. This compound does not activate C—H bonds in benzene, alkenes or diethyl ether.

d. Complexes with monoanionic N,O-containing amide ligands

Bidentate monoanionic amide ligands containing an additional donor group, $[Me_2Si(NBu^t)(OBu^t)]^-$ (L), have been proposed for the first time as an alternative to cyclopentadienyl ligands.[50, 51] The monomeric five-coordinate yttrium complex $L_2YCH(SiMe_3)_2$ (**33**) was synthesised by the exchange reaction of chloride $L_2Y(\mu\text{-}Cl)_2Li(THF)_2$ with $(Me_3Si)_2CHLi$. Compound **33** reacts with hydrogen in THF to give unstable hydride $[L_2Y(\mu\text{-}H)]_2$, which was characterised in solution by ^1H and ^{13}C NMR spectroscopy. The reactions of complex **33** with alkynes RC≡CH (R = Me_3Si or Bu^t) are accompanied by the Y—C and Y—N bond cleavage to form acetylenides $(RC{\equiv}C)_3Y$; however, PhC≡CH undergoes polymerisation in this reaction. The reaction of derivative **33** with excess of MeC≡N is accompanied by the C—H bond activation and elimination of bis(trimethylsilyl)methane. The subsequent insertion of one equivalent of MeC≡N at the Y—C bond and the 1,3-proton shift give rise to complex **34** (Scheme 4). The C—H bond activation was observed also in the reactions of complex **33** with pyridine, methylpyridine and ethylpyridine. The X-ray diffraction study of complexes **33** and **34** showed that this ligand system is bulkier than the η^5-C_5Me_5 ligand.

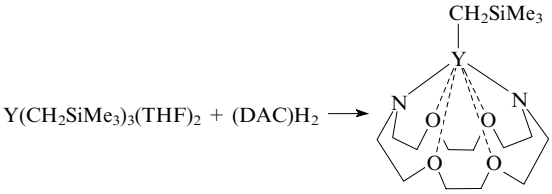
e. Complexes with dianionic N,O-containing diamide ligands

The tridentate dianionic ligand containing two oxygen-bridged amido-containing fragments, $[2\text{-}Bu^tNC_6H_4)_2O]^{2-}$, was used [52] for the synthesis of five-coordinate yttrium complex **35**. The structure of the latter was determined by X-ray diffraction.



35

Doubly deprotonated 4,13-diaza-18-crown-6 (DAC) proved to be suitable coordination environment for the synthesis of the yttrium derivative (DAC)YCH_2SiMe_3 (**36**).[53, 54]



36

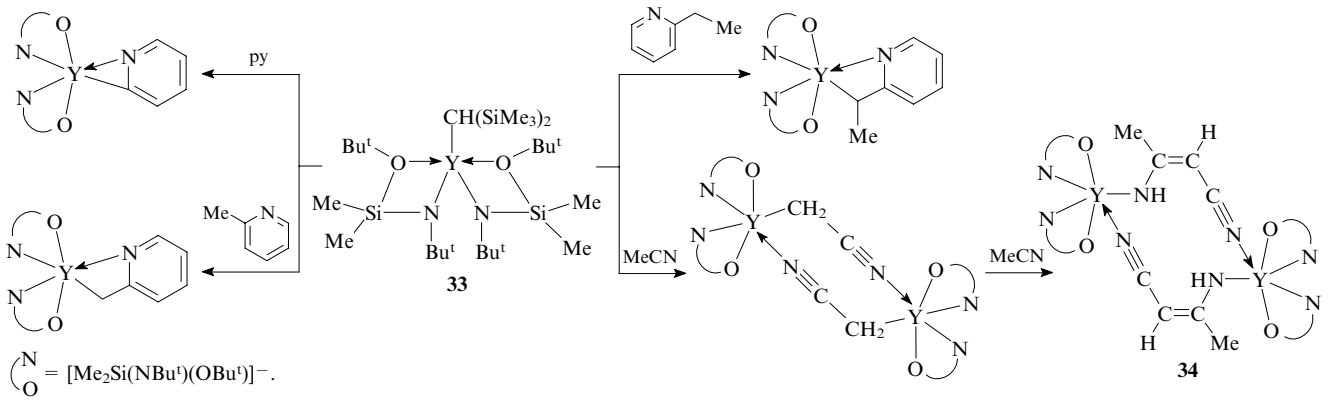
The reaction of complex **36** with phenylacetylene produces an equilibrium mixture of butatrienediyl {[(DAC)Y]$_2$Y.(μ-PhC=C=C=CPh)} and dimeric acetylenide ([(DAC)Y(μ-C≡CPh)]$_2$) complexes.

f. Complexes with monoanionic N,P-containing amide ligands

Being soft Lewis bases, neutral phosphines are considered as unsuitable ligands for coordination to hard rare-earth metal ions.[55] The coordination of the phosphine groups to rare-earth metal atoms was achieved with the use of the monoanionic amide ligand $[N(SiMe_2CH_2PMe_2)_2]^-$ containing two PMe_2 fragments in the side chains (Scheme 5).

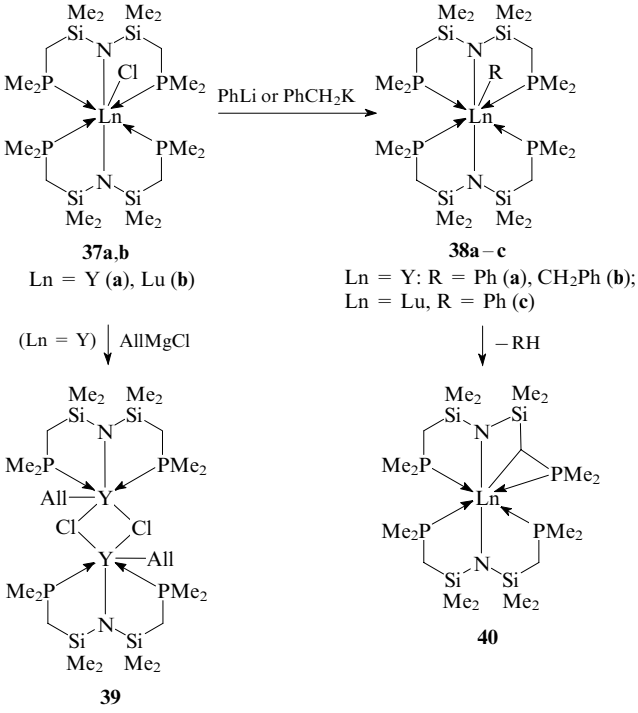
The exchange reaction involving yttrium or lutetium chloro complexes (**37**) and phenyllithium or benzylpotassium produced [56, 57] the corresponding derivatives **38a**–**c**. An attempt to synthesise [58] allyl derivatives of yttrium by the reaction of complex **37a** with AllMgCl led to the replacement of one of the amide ligands to form compound **39**, rather than to the expected substitution of the chlorine atom. Complexes **38a**–**c** are thermally unstable and are involved in cyclometallation at the methylene group to give metallacyclic derivative **40**.[59]

Scheme 4



$\begin{pmatrix} N \\ O \end{pmatrix}$ = $[Me_2Si(NBu^t)(OBu^t)]^-$.

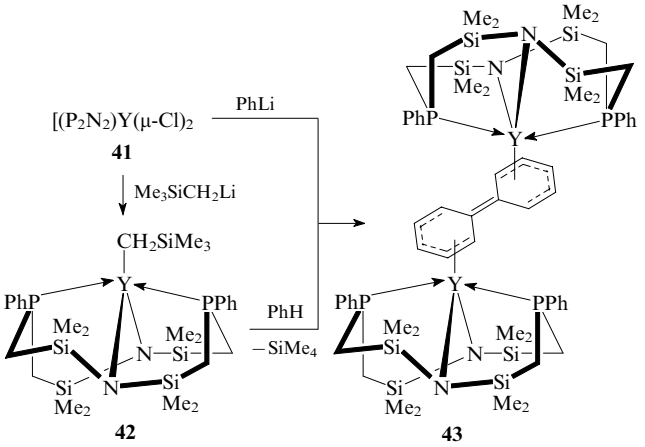
Scheme 5



g. Complexes with dianionic N,P-containing amide ligands

The macrocyclic dianionic bis(amidophosphine) ligand $[PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh]^{2-}$ (P_2N_2) was used for the synthesis of rare-earth metal alkyl and aryl complexes. The reactions of $[(P_2N_2)Ln(\mu\text{-}Cl)]_2$ (Ln = Y (**41**), Ho, Yb or Lu) with $(Me_3Si)_2CHLi$ and Me_3SiCH_2Li in toluene produce the corresponding derivatives $(P_2N_2)LnR$ [Ln = Y, R = $CH(SiMe_3)_2$, CH_2SiMe_3 (**42**); Ln = Ho, R = CH_2SiMe_3; Ln = Yb, R = CH_2SiMe_3; Ln = Lu, R = CH_2SiMe_3], whereas the arylation of these complexes strongly depends on the ionic radius of the metal atom.[60,61] For example, the reactions of Y and Ho complexes with phenyllithium and biphenylyllithium are accompanied by the dimerisation of aryl radicals to form the dinuclear complexes $[(P_2N_2)_2Ln]_2.(\mu\text{-}\eta^6\text{:}\eta^6\text{-}Ph_2)$ [Ln = Y (**43**) or Ho] and $[(P_2N_2)_2Y]_2[\mu\text{-}\eta^6\text{:}\eta^6\text{-}(C_6H_4\text{-}Ph\text{-}p)_2]$ containing the biphenyl or quaterphenyl dianion, respectively (Scheme 6).

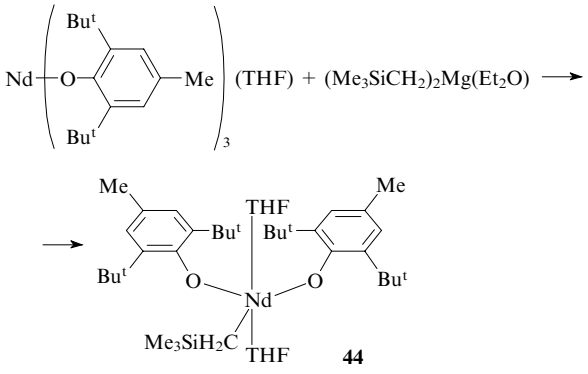
Scheme 6



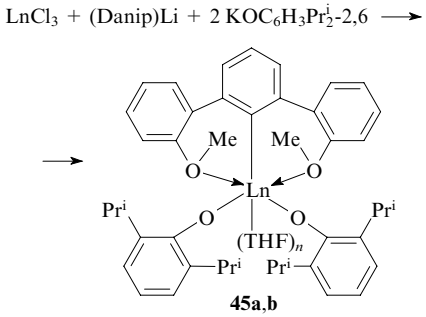
The slow transformation of complex **42** into dimer **43** in benzene at room temperature accompanied by elimination of tetramethylsilane was observed. For ytterbium having a smaller ionic radius, the phenyl derivative $(P_2N_2)_2YbPh$ was isolated and characterised by X-ray diffraction. The presence of THF appeared to be the decisive factor for the suppression of the dimerisation of the aryl radicals. For example, the yttrium aryl complex was isolated as the adduct with THF, $(P_2N_2)Y(C_6H_4Me\text{-}4)(THF)$, in the reaction of $[(P_2N_2)Y.(\mu\text{-}Cl)]_2$ with *p*-tolyllithium in a toluene–THF mixture.[61]

h. Complexes with monoanionic alkoxide ligands

The five-coordinate neodymium alkyl complex $L_2Nd.(CH_2SiMe_3)(THF)_2$ (**44**) containing two sterically hindered phenoxide ligands L was obtained in a mixture with the derivative $LNd(CH_2SiMe_3)_2$ by the reaction of neodymium tris(phenoxide) with the corresponding magnesium derivative in a toluene–THF mixture.[62] The structure of complex **44** was confirmed by X-ray diffraction.



Yttrium compound **45a** and ytterbium compound **45b** with the Danip ligand containing two *o*-anisole fragments were synthesised by the successive exchange reactions of $LnCl_3$ with one equivalent of (Danip)Li and two equivalents of $KOC_6H_3Pr^i_2$-2,6 in THF.[63] In complex **45b**, the ytterbium coordination sphere involves one carbon atom and two oxygen atoms of the 2,6-di(*o*-anisolyl)phenyl fragment and two oxygen atoms of the 2,6-diisopropylphenoxide ligands, *i.e.*, the coordination number is 5. The compound of yttrium having a larger ionic radius[64] was isolated as the adduct with THF (**45a**); the coordination number of the metal atom in this adduct is 6.



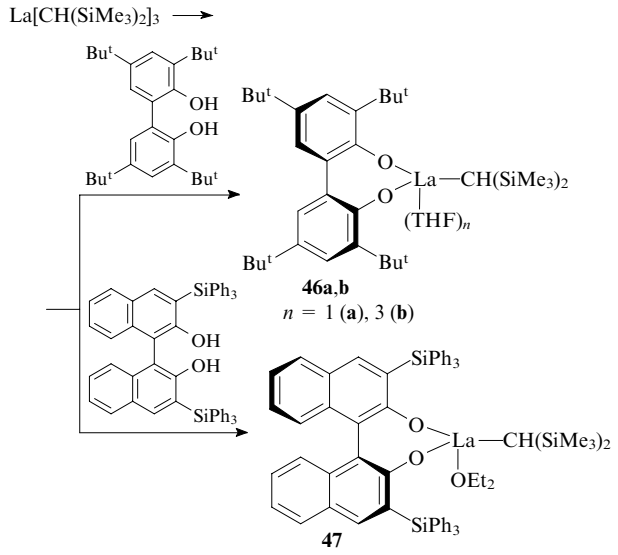
Ln = Y, *n* = 1 (**a**); Ln = Yb, *n* = 0 (**b**).

i. Complexes with dianionic alkoxide ligands

Derivatives containing biphenyl-2,2′-diolate and 1,1′-binaphthyl-2,2′-diolate anions represent complexes with dianionic alkoxide ligands. Compounds **46** and **47** were synthesised for the first time[65] by the reaction of substituted biphenyldiol or binaphthyldiol with the $La[CH(SiMe_3)_2]_3$ complex (Scheme 7).

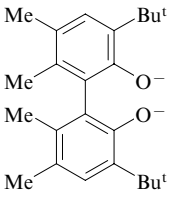
The reaction of complex **47** with CO is accompanied by the insertion of the latter at the La–C bond followed by the 1,2-

Scheme 7

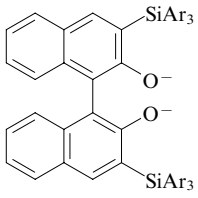


migration of the $SiMe_3$ group to form enolate [1,1′-(2-$OC_{10}H_5$.$SiPh_3$-3)$_2$]La[OC($SiMe_3$)=CHSiMe_3].[65]

An analogous approach was used for the preparation of rare-earth metal alkyl and aryl complexes containing the enantiomerically pure (*R*)-Biphen[66] and (*R*)-Binol-$SiAr_3$ ligands.[67,68]

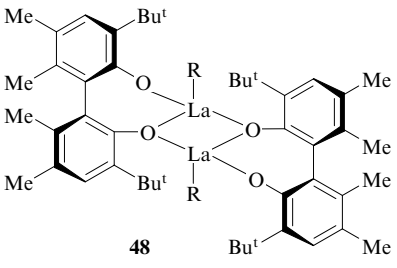


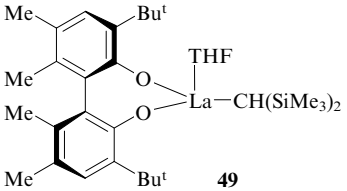
Biphen



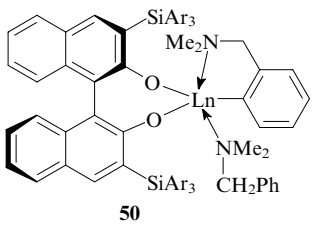
Binol-$SiAr_3$

Complex **48** was isolated[66] as the dimer formed by two bridging aryloxide groups. The treatment of this complex with excess THF leads to dissociation of the dimer and the formation of adduct **49**.[66]



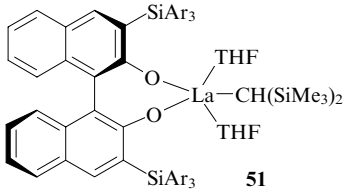


The Binol-$SiAr_3$ derivatives are monomeric.[67,68] Compounds **50** and **51** can be given as examples.



50

Ln = Sc, Y, Lu; Ar = Ph, 3,5-$Me_2C_6H_3$.

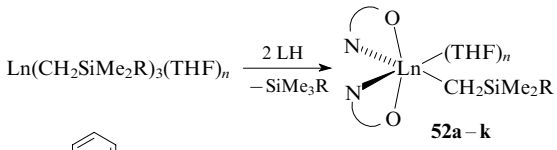


51

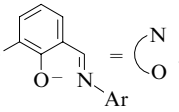
Ar = Ph, 3,5-$Me_2C_6H_3$.

j. Complexes with monoanionic N,O-alkoxide ligands

Among bidentate N,O-alkoxide ligands, salicylaldiminate ligands are most widely used in the synthesis of alkyl derivatives. The elimination of substituted alkane in the reactions of 2-iminomethylphenols with trialkyl derivatives was demonstrated[69–71] to be a convenient procedure for the preparation of such complexes, whereas the exchange reactions do not produce the target compounds in good yield. The reactions of the Ln(CH_2SiMe_2R)$_3$(THF)$_n$ compounds (Ln = Sc or Y; R = Me or Ph; *n* = 1 or 2) with two equivalents of 2-iminomethylphenol LH afford complexes **52a**–**k** in high yields.[69–71]

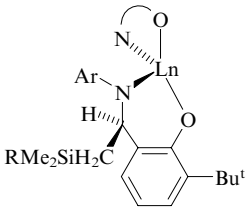


52a–**k**

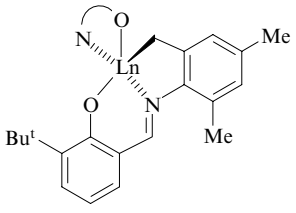
L = 

Compound **52**	Ln	Ar	R	*n*
a	Sc	Ph	Ph	1
b	Y	Ph	Ph	2
c	Sc	2-Pr^{i}C$_6$H$_4$	Ph	1
d	Y	2-Pr^{i}C$_6$H$_4$	Ph	1
e	Sc	Mes	Me	0
f	Y	Mes	Ph	1
g	Y	Mes	Me	0
h	Sc	2,6-Pr$^i_2$C$_6$H$_3$	Me	0
i	Sc	2,6-Pr$^i_2$C$_6$H$_3$	Ph	0
j	Y	2,6-Pr$^i_2$C$_6$H$_3$	Ph	0
k	Y	2,6-Pr$^i_2$C$_6$H$_3$	Me	0

Thermal stability of the reaction products substantially depends on the bulkiness of the substituent at the nitrogen atom. The complexes with the substituents Ar = Ph, 2-Pr^{i}C$_6$H$_4$ or Mes are unstable and slowly decompose in the temperature range from −20 to +20 °C, in the case of Ar = Ph or 2-Pr^{i}C$_6$H$_4$ the decomposition being accompanied by the migration of the CH_2SiMe_2R group to the aldimine carbon atom (structure **A**), whereas the *ortho*-methyl substituents of the aryl group are metallated in the case of Ar = Mes (structure **B**).[70]



A



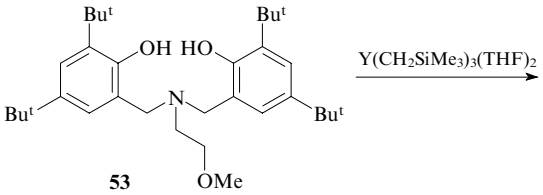
B

On the contrary, five-coordinate derivatives of the bulkiest ligand with Ar = 2,6-$Pr^i_2C_6H_3$ (compounds **52h–k**) are characterised by high thermal stability and decompose in the toluene solvent only upon prolonged heating at 140 °C. This reaction is accompanied by metallation of one methyl group of the isopropyl substituent.[71]

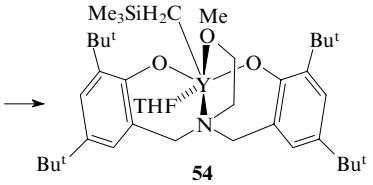
The reaction of the trialkyl complex $Y(CH_2SiMe_3)_3(THF)$ with iminomethylphenol 2-(CyN=CH)-6-$Bu^tC_6H_3OH$ (LH) produced the monoalkyl yttrium derivative $L_2Y(CH_2SiMe_3)$.(THF) even when the starting compounds were taken in equimolar amounts.[72]

k. Complexes with dianionic N,O-alkoxide ligands

In recent years, sterically hindered polydentate bis(phenoxide) ligands containing additional donor groups capable of coordinating to metal atoms have found wide use in the chemistry of rare-earth organometallic compounds. The reaction of $Y(CH_2SiMe_3)_3(THF)_2$ with bis(phenol) **53** was demonstrated[73] to proceed selectively to give six-coordinate yttrium complex **54** in good yield.



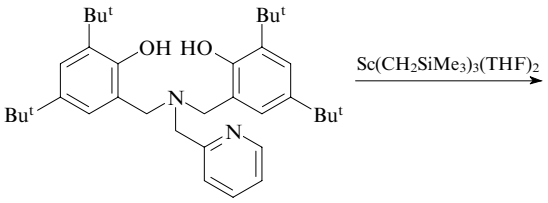
53

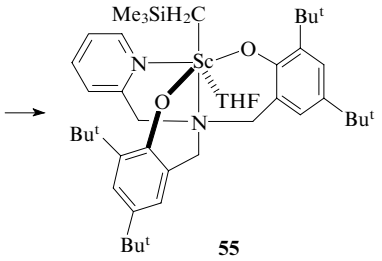


54

The X-ray diffraction and NMR spectroscopic data provide evidence that the methoxy group is coordinated to the metal atom in complex **54** both in the crystalline state and in nonpolar solvents. It should be noted that complex **54** is inactive in the ethylene polymerisation.

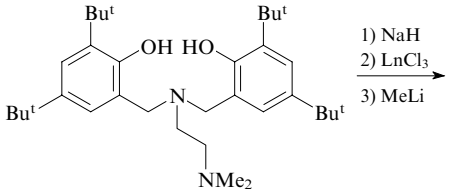
An analogous approach was used[74] for the synthesis of scandium complex **55** with the bis(phenoxide) ligand containing the tertiary amine and pyridine groups.

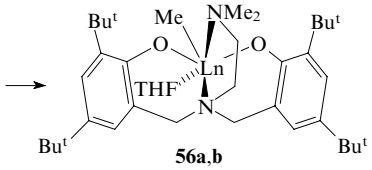




55

Erbium and ytterbium complexes (**56a**,**b**) with the related bis(phenoxide) ligand containing two amino groups were synthesised from metal trichlorides by the successive exchange reactions. The structure of compound **56b** was established by X-ray diffraction.[75]

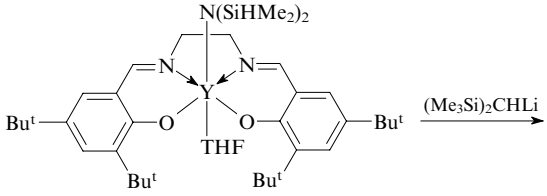


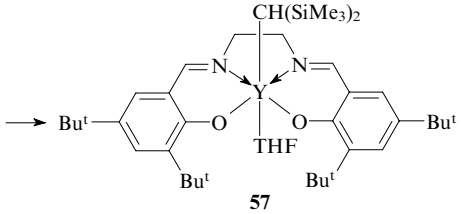


56a,**b**

Ln = Er (**a**), Yb (**b**).

Yttrium alkyl complex **57** stabilised by the substituted tetradentate *N*,*N*′-ethylenebis(salicylaldiminate) ligand was also prepared by the exchange reaction; however, the bis(dimethylsilyl)amide fragment was used in the latter case as the leaving group.[76]





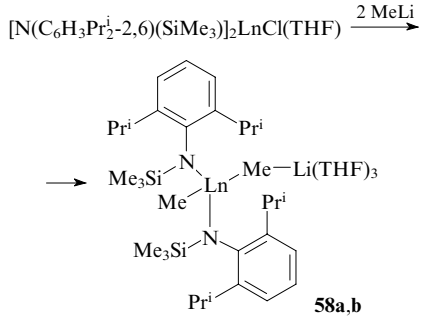
57

2. Heterobimetallic alkyl complexes

a. Complexes with monoanionic N-containing ligands

Monoanionic monodentate amide ligands have found little use in the synthesis of alkyl derivatives of rare-earth elements. The sterically hindered *N*-(2,6-diisopropylphenyl)trimethylsilylamide ligand was used[77] for the first time for the preparation of the bis(arylamido) chloride complexes $[N(C_6H_3Pr^i_2\text{-}2,6).(SiMe_3)]_2LnCl(THF)$ (Ln = Nd or Yb). The reactions of these compounds with methyllithium (in a molar ratio of 1 : 2) in a toluene–diethyl ether mixture produce ate complexes **58a**,**b**.[78] The X-ray diffraction study showed that only one of

two methyl groups serves as a bridge between the lanthanide and lithium atoms.



58a,b

Ln = Nd (**a**), Yb (**b**).

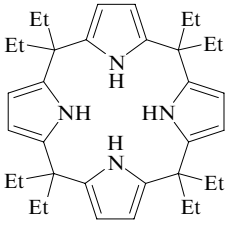
Ate complexes containing monoanionic bidentate amidinate and guanidinate ligands, $L_2Ln(\mu\text{-}Me)_2Li(TMEDA)$ [L = $PhC(NSiMe_3)_2$, Ln = Y (**59a**);[26] L = $(Me_3Si)_2NC(NPr^i)_2$, Ln = Y,[29] Nd (**59b**), Yb (**59c**);[79,80] L = $(Me_3Si)_2NC(NCy)_2$, Ln = Y;[30] TMEDA is *N*,*N*,*N*′,*N*′-tetramethylethylenediamine], were synthesised by the reactions of the corresponding chlorides $[L_2Ln(\mu\text{-}Cl)]_2$ or $L_2Ln(\mu\text{-}Cl)_2Li(B)_n$ (B = THF, DME or Et_2O) with two equivalents of MeLi in the presence of excess TMEDA. The reaction of complex **59a** with $Bu^tC{\equiv}CH$ afforded the corresponding heterobimetallic acetylenide $L_2Y(\mu\text{-}C{\equiv}CBu^t)_2Li(TMEDA)$.

b. Complexes with dianionic amide ligands and N-containing macrocycles

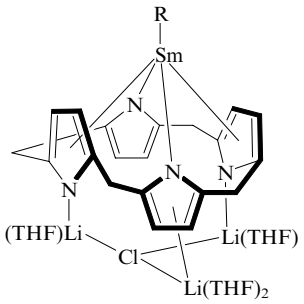
The synthesis of derivatives of the dianionic tridentate 2,6-diiminopyridine ligand, in which the neodymium and lithium atoms are linked by two bridging methyl ligands or one methyl ligand and one chloride ligand, respectively, [2,6-{2,6-$Pr^i_2C_6H_3NC(=CH_2)\}_2C_5H_3N$]Nd(μ-Me)(μ-X)[$Li(THF)_2$] (X = Me or Cl), was documented.[39]

The octaethylporphyrin derivative of yttrium (OEP)Y.$(\mu\text{-}Me)_2Li(OEt_2)$, which was synthesised[47,81] by the reaction of phenoxide (OEP)Y($OC_6H_3Bu^t_2$-2,6) with MeLi (in a ratio of 1 : 2), belongs to heterobimetallic alkyl complexes with dianionic N-containing ligands.

Trivalent samarium methyl and vinyl complexes **60a,b** with the octaethylcalix-tetrapyrrole ligand (Et_8-calix-pyrrole) were synthesied[82] by the reactions of chloride (Et_8-calix-pyrrole).SmCl[$Li_2(THF)_3$] with the corresponding lithium reagents RLi (R = Me, $CH_2{=}CH$). The alkylation of the dinuclear complex (Et_8-calix-pyrrole)$Sm_2\{(\mu\text{-}Cl)_2[Li(THF)_2]\}_2$ affords tetramethyl complex **61**.[83] (The ethyl groups in structures **60** and **61** are omitted for clarity.)

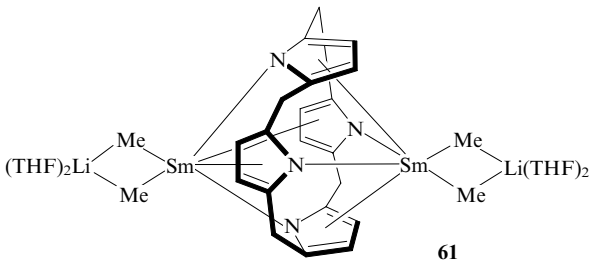


Et_8-calix-pyrrole



60a,b

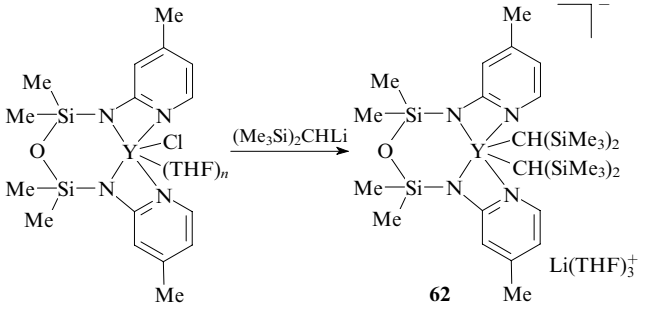
R = Me (**a**), $CH_2{=}CH$ (**b**)



61

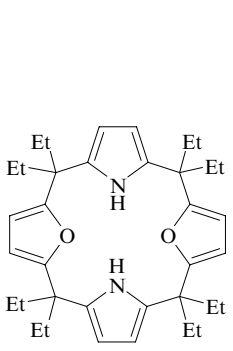
c. Complexes with dianionic N,O-containing diamide ligands

The tetradentate ligand, in which two 2-amino-4-methylpyridine (Ap) fragments are linked by the siloxane bridge $O(SiMe_2)_2$, was used[84] for the synthesis of heterobimetallic yttrium complex **62**.

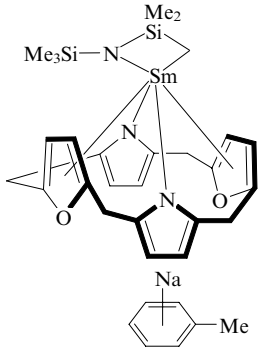


62

In the study of the reaction of the Sm^{III} bis(trimethylsilyl)-amide complex ontaining the *trans*-dioxaporphyrinogen ligand (PORFO) with amide $NaN(SiMe_3)_2$,[85] the process was found to be accompanied by activation of one C—H bond of the trimethylsilylamide group and produces metallacyclic γ-alkylamide complex **63** (the ethyl groups are omitted).



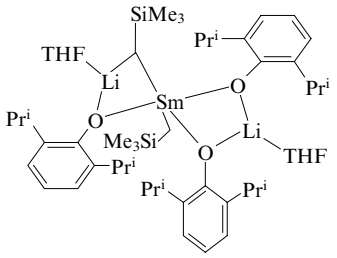
(PORFO)H_2



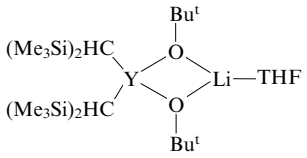
63

d. Complexes with alkyl- and aryloxide ligands

The reaction of $Sm(OC_6H_3Pr^i_2\text{-}2,6)_3$ with three equivalents of Me_3SiCH_2Li in toluene produced heterobimetallic trinuclear samarium complex **64**,[86] in which the metal atom is coordinated by one terminal CH_2SiMe_3 group, one bridging CH_2SiMe_3 group and three bridging aryloxide ligands (coordination number of Sm is 5).

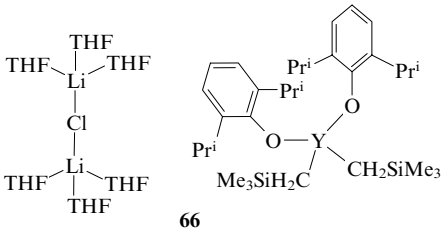


64

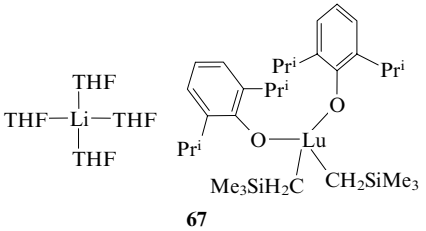


65

Bimetallic four-coordinate yttrium complex **65** was synthesised [87] by two successive exchange reactions of YCl_3 with two equivalents of $(Me_3Si)_2CHLi$ and two equivalents of $LiOBu^t$. The structures of complexes **64** and **65** were established by X-ray diffraction. The coordination environment of the yttrium atom can be described as a distorted tetrahedron formed by two terminal $CH(SiMe_3)_2$ groups and two bridging *tert*-butoxide groups. The formation of yttrium ate complex **66**, which is a separated ion pair, was observed [88] in the reaction of YCl_3 with Me_3SiCH_2Li and $LiOC_6H_3Pr^i_2$-2,6 (in a ratio of 1 : 2 : 2). The analogous reaction of the lutetium complex also produced ionic complex **67** consisting of the discrete cation and anion; however, this complex does not contain LiCl. It should be noted that complex **66** contains the unusual $[\{Li(THF)_3\}_2Cl]^+$ cation.



66



67

The formation of the heterodinuclear complex $Li[Y(OSiBu^tAr_2)(OC_6H_3Bu^t_2\text{-}2,6)(CH_2SiMe_3)_2]$ ($Ar = C_6H_4.CH_2NMe_2$-2) by the reaction of the derivative $Y(OSiBu^tAr_2)(OC_6H_3Bu^t_2\text{-}2,6)_2$ with two equivalents of Me_3SiCH_2Li was documented.[89]

e. Adducts of rare-earth metal complexes with trialkylaluminium

Due to the catalytic activity of the Ziegler–Natta systems based on rare-earth metal complexes in the alkene and diene polymerisation, considerable attention has been given to the reactions of their tris(amides) and tris(alkoxides) with various trialkyl derivatives of aluminium. These reactions produce heterobimetallic complexes containing the Ln–C bond. The reaction of $Nd(NPr^i_2)_3(THF)$ with 3 equivalents of $AlMe_3$ was found [90] to be accompanied by the Nd–C bond formation to give the heterobimetallic trinuclear complex with three bridging methyl groups, $Nd(NPr^i_2)[(\mu\text{-}Me)AlMe_2][(\mu\text{-}Me)_2AlMe_2]$. The seven-coordinate neodymium complex $[\{Me_2Al(\mu\text{-}Me)_2\}_2.Nd(\mu_3\text{-}NPh)(\mu\text{-}Me)AlMe]_2$ containing the μ_3-imide ligand was synthesised [91] by the reaction of $[Nd(NHPh)_3(KCl)_3]$ with Al_2Me_6. Four sites in the neodymium coordination sphere are occupied by two chelating anions $[(\mu\text{-}Me)AlMe_2]^-$, and three sites are occupied by the tridentate group $(\mu_3\text{-}NPh)(\mu\text{-}Me).AlMe$. The yttrium octaethylporphyrin complex (OEP)Y.$(\mu\text{-}Me)_2AlMe_2$ was synthesised [47,81] by the reaction of 2 equivalents of $AlMe_3$ with $(OEP)Y(\mu\text{-}Me)_2Li(OEt_2)$.

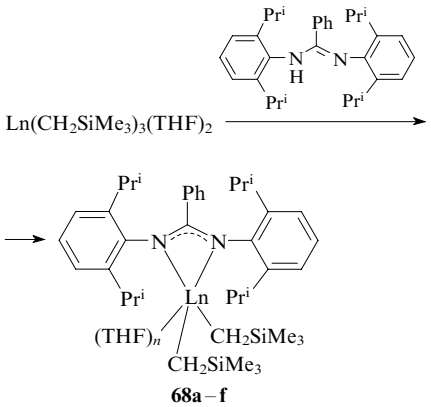
Studies of the reactions of lanthanide aryloxides with AlR_3 showed that they can produce adducts of different composition depending on the bulkiness of the ArO group and the ionic radius of the lanthanide atom. For example, the reaction of $Ln(OC_6H_3Pr^i_2\text{-}2,6)_3$ with AlR_3 (in a ratio of 1 : 4) produced the trinuclear complexes $Ln(OC_6H_3Pr^i_2\text{-}2,6)[(\mu\text{-}OC_6H_3Pr^i_2\text{-}2,6).(\mu\text{-}R)AlR_2]_2$ [Ln = La or Sm; R = Me or Et;[92,93] Ln = Y, R = Me (Ref. 94)]. Lanthanum aryloxide containing the bulkier 2,6-di-(*tert*-butyl)phenoxide groups OAr (Ar = $C_6H_3.Bu^t_2$-2,6 or $C_6H_2Bu^t_2$-2,6-Me-4) reacts with $AlMe_3$ to form the dinuclear complex $La(OAr)_3(AlMe_3)$.[94] The reactions of aryloxides of rare-earth metals having a smaller ionic radius produce the monotetramethylaluminate complexes $Ln(OAr)_2.[(\mu\text{-}Me)_2AlMe_2]$ (Ln = Y or Lu; Ar = $C_6H_3Bu^t_2$-2,6, $C_6H_2Bu^t_2$-2,6-Me-4 or $C_6H_2Bu^t_3$-2,4,6).[94] The reaction of the trinuclear complex $Y_3(OBu^t)_7Cl_2(THF)_2$ with $AlMe_3$ in hexane afforded [95] bimetallic complexes, in which the yttrium and aluminium atoms are linked by the bridging methyl ligands $Y[(\mu\text{-}OBu^t)(\mu\text{-}Me)AlMe_2]_3$ or $(Bu^tO)(THF)Y[(\mu\text{-}OBu^t)(\mu\text{-}Me).AlMe_2]_2$. The mono- and bis(tetraalkylaluminate) complexes $[Me_2Al(O_2CC_6H_2Pr^i_3\text{-}2,4,6)_2]_2Ln[(\mu\text{-}Me)_2AlMe_2]$ and $\{Ln(O_2CC_6H_2Bu^t_3\text{-}2,4,6)[(\mu\text{-}Me)_2AlMe_2]_2\}_2$ were synthesised [96,97] by the alkylation of rare-earth carboxylates $[Ln(O_2CC_6H_2R_3\text{-}2,4,6)_3]_n$ (R = Me, Pr^i or Bu^t; Ln = Y, La or Nd) with trialkylaluminium AlR_3 (R = Me or Et).

3. Dialkyl and diaryl complexes

Rare-earth metal dialkyl complexes have attracted increasing attention as the starting compounds for the synthesis of cationic alkyl derivatives serving as active alkene polymerisation and co-polymerisation catalysts.[98,99] Half-sandwich dialkyl complexes were considered in special sections of recent reviews.[100,101]

a. Complexes with monoanionic N-containing ligands

The synthesis, structures and reactivities of yttrium, scandium and lanthanide dialkyl complexes (**68a–f**) stabilised by bulky benzamidinate ligands were documented.[102,103] The complexes were synthesised by elimination of tetramethylsilane in the reactions of amidine with the trialkyl compounds $Ln(CH_2SiMe_3)_3(THF)_2$. Derivatives of metals having a smaller ionic radius contain one coordinated THF molecule (compounds **68b**,**f**), whereas the coordination number of the central atom in complexes of metals with larger ionic radii (**68a**,**c–e**) increases to 6 as a result of coordination of an additional THF molecule.

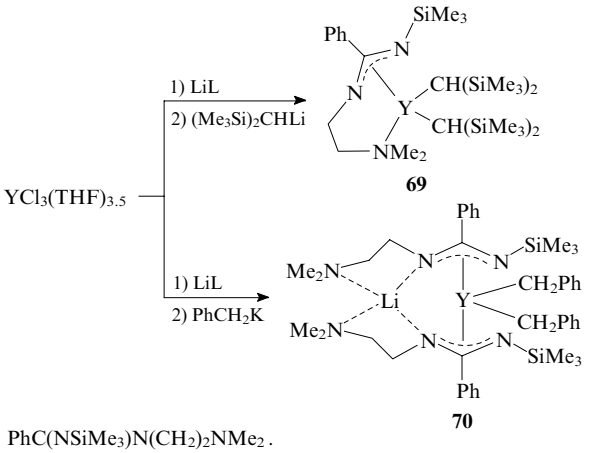


68a–f

Ln = Y (**a**), Sc (**b**), La (**c**), Nd (**d**), Gd (**e**), Lu (**f**); *n* = 1 (**b**, **f**), 2 (**a**, **c–e**).

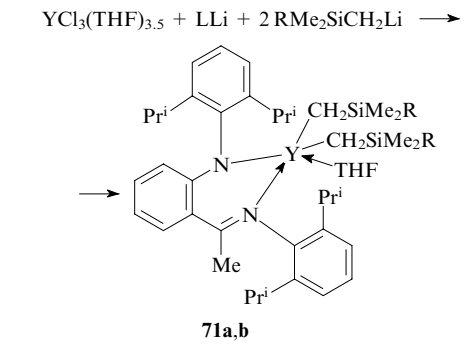
Yttrium dialkyl complex **69** can also be prepared by the exchange reaction with a less bulky tridentate amidinate ligand containing an additional amino group in the substituent.[33] An

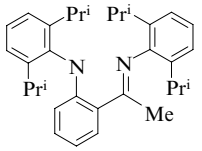
attempt to apply this procedure to the synthesis of the dibenzyl derivative led to the formation of ate complex **70**, in which the Y and Li atoms have the coordination numbers 6 and 4, respectively. Therefore, a decrease in the volume of the σ-bonded ligand (CH_2Ph instead of $CH(SiMe_3)_2$) leads to substantial changes in the coordination environment of the Y atom. Thus, the amidinate ligands are coordinated only by two N atoms, whereas the nitrogen atom of the amino group is coordinated to the lithium ion.



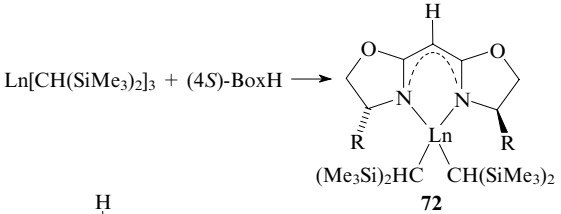
L = $PhC(NSiMe_3)N(CH_2)_2NMe_2$.

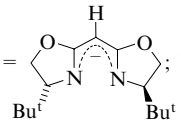
A bidentate anilido-imine ligand was used [104] for the synthesis of yttrium dialkyl complexes **71a**,**b**.



L =  ; R = Me (**a**), Ph (**b**).

A series of lanthanide dialkyl complexes **72** containing the chiral bidentate bis(oxazoline) ligands (Box) were synthesised *in situ* by elimination of alkane from the corresponding derivatives $Ln[CH(SiMe_3)_2]_3$ in the reactions with BoxH. The lutetium complex was isolated from the reaction mixture and its structure was established by X-ray diffraction.[105]



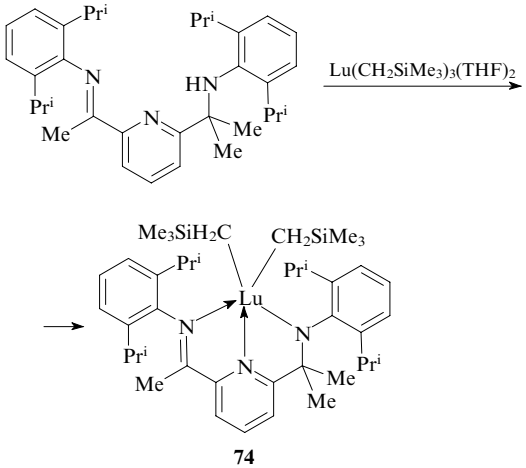
Box =  ; Ln = La, Nd, Sm, Y, Lu.

β-Diketiminate ligands have found wide use in the synthesis of four-coordinate scandium dialkyl complexes. The $[ArNC(R^1)CHC(R^1)NAr]ScR^2_2(THF)_n$ complexes (**73a**–**i**) (Ar = 2,6-$Pr^i_2C_6H_3$) were synthesised [106, 107] by the alkylation of the corresponding dichlorides $[ArNC(R^1)CHC(R^1).NAr]ScCl_2(THF)_n$ (n = 0 or 1).

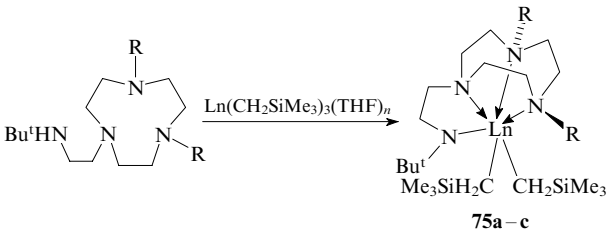
Compound **73**	R^1	R^2	Compound **73**	R^1	R^2
a	Me	Me	**f**	Me	CH_2Bu^t
b	Me	CH_2Ph	**g**	Bu^t	CH_2Bu^t
c	Bu^t	Me	**h**	Me	CH_2SiMe_3
d	Bu^t	Et	**i**	Bu^t	CH_2SiMe_3
e	Bu^t	CH_2Ph			

It should be noted that only derivative **73a** ($R^1 = R^2$ = Me) contains one coordinated THF molecule. For derivatives bearing larger substituents R^1 and R^2, $n = 0$. This synthetic approach allows the preparation of the mixed alkyl derivatives $[ArNC(Bu^t)CHC(Bu^t)NAr]ScMe(CH_2.SiMe_3)$ and dialkyl derivatives containing no coordinated Lewis bases. The high potential of these ligands in stabilisation of rare-earth organometallic compounds is demonstrated by the fact that even diethyl derivatives, which are generally very unstable because of the tendency to undergo β-hydride elimination, can be isolated in the presence of β-diketiminate ligands. The structures of complexes **73a**,**c**,**e**,**h**,**i** were established by X-ray diffraction. The dimeric dimethyl complex $[\{ArNC(Me)CHC(Me)NAr\}ScMe_2]_2$ is involved in the disproportionation with dichloride $[\{ArNC(Me)CHC(Me).NAr\}ScCl_2]_2$ to give the alkyl chloride derivative $[\{ArNC.(Me)CHC(Me)NAr\}ScClMe]_2$.[108] The reactions of complexes **73h**,**i** with $Bu^nP{=}Te$ are accompanied by the insertion of the tellurium atom at the Ln–C bond to form the corresponding tellurolates $[ArNC(Me)CHC(Me)NAr]Sc(TeCH_2SiMe_3)_2$.[109]

The synthesis and structure of lutetium complex **74** containing the tridentate anilido-pyridine-imine ligand were documented.[110]

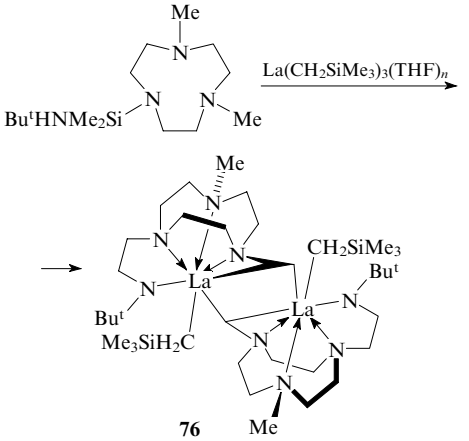


Recently, monoanionic tetradentate amide ligands have been designed [111, 112] and used in the synthesis of yttrium (**75a**,**b**) and lanthanum (**75c**) dialkyl complexes. It should be noted that the use of a ligand in which the 1,4,7-triazacyclononane and amide fragments are dimethylene-bridged allows the isolation of the lanthanum dialkyl complex. In the case of the ligand containing the shorter silylene ($SiMe_2$) bridge, the reaction is accompanied by the metallation of one methyl group resulting in the formation of dimer **76**.



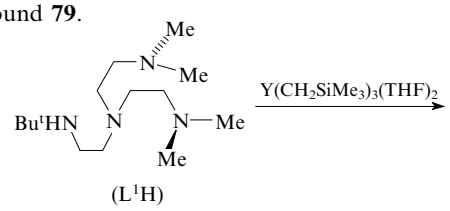
75a–c

Ln = Y: R = Me (**a**), Pr^i (**b**); Ln = La, R = Me (**c**).

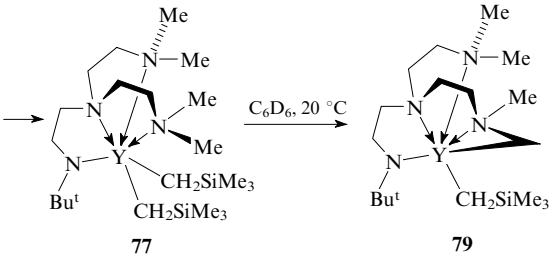


76

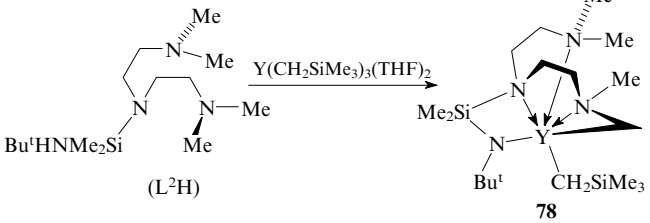
The monoanionic tetradentate ligands $[(Me_2NCH_2CH_2)_2N-X-NBu^t]^-$ [X = $(CH_2)_2$ (L^1) or $SiMe_2$ (L^2)], in which three neutral amine fragments are not linked together to form a rigid ring, were used [113] for the synthesis of yttrium derivatives. The reaction of L^1H with $Y(CH_2SiMe_3)_3(THF)_2$ produces complex **77**, whereas the reaction of this starting compound with L^2H is accompanied by the rapid metallation of one methyl group to form metallacyclic product **78**. The C–H bond activation was observed also upon storage of compound **77** in deuterobenzene at room temperature for 8 h resulting in the formation of compound **79**.



(L^1H)



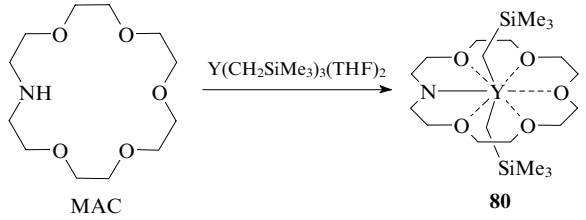
77 **79**



(L^2H) **78**

The synthesis of yttrium dialkyl and diphenyl complexes containing the dimethyl tris(pyrazolyl)borate ligands TPB-Me_2 and (TPB-Me_2)YR_2(THF) (R = Me, Bu^t, CH_2SiMe_3 or Ph) was documented.[114] Unfortunately, these compounds were characterised only by spectroscopic methods and elemental analysis.

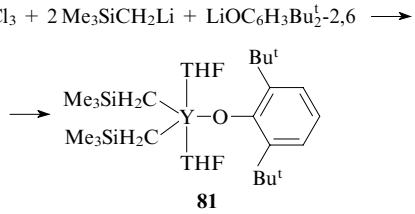
The deprotonation of aza-18-crown-6 (MAC) with the yttrium derivative $Y(CH_2SiMe_3)_3(THF)_2$ affords complex **80** in which the metal atom is located in the centre of the cavity of the hexadentate macrocyclic ligand, and the CH_2SiMe_3 groups are in axial positions.[115]



MAC **80**

b. Complexes with monoanionic O-containing ligands

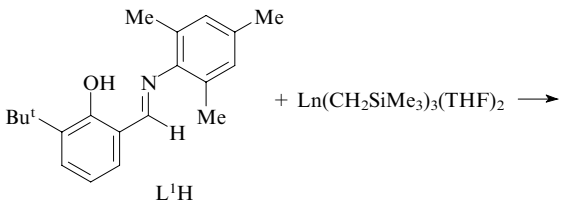
The only dialkyl derivative containing an aryloxide ligand is known. An X-ray diffraction study showed [87] that compound **81** exists as a monomer in the crystalline state.



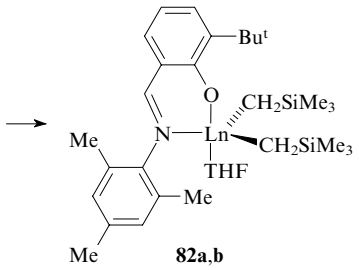
81

c. Complexes with monoanionic N,O-containing aryloxide ligands

Salicylaldiminate ligands containing substituents of different bulkiness in the aromatic rings of the phenol and imine fragments were used for the synthesis of scandium and yttrium dialkyl complexes. The reactions of equimolar amounts of the $Ln(CH_2SiMe_3)_3(THF)_2$ compounds (Ln = Sc or Y) with the 2-(MesN=CH)-6-Bu^{t}C$_6$H$_3$OH (L^1H) ligand produce trigonal-bipyramidal five-coordinate complexes **82a**,**b**. Scandium compound **82a** is stable in a toluene solution at room temperature, whereas yttrium analogue **82b** undergoes disproportionation to form the homoligand complex L^1_3Y. The scandium derivative $L^2Sc(CH_2SiMe_3)_2(THF)$ was isolated also in the reaction with the iminomethylphenol 2-(CyN=CH)-6-Bu^{t}C$_6$H$_3$OH (L^2H).[72] The reaction of L^2H with the yttrium compound produces the six-coordinate complex $L^2_2Y(CH_2SiMe_3)(THF)$ containing two phenoxy-imine ligands and one CH_2SiMe_3 group regardless of the reactant molar ratio.



L^1H

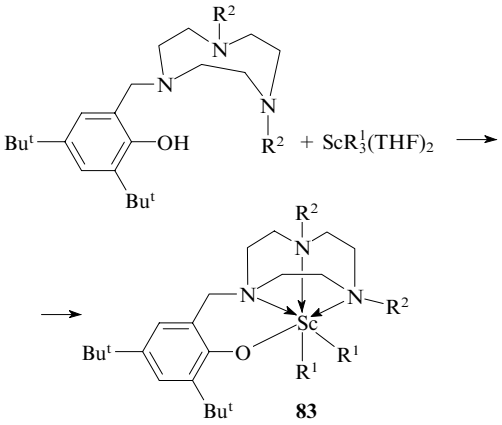


82a,**b**

Ln = Sc (**a**), Y (**b**).

The related ligand with the bulkier diisopropylphenyl substituent at the nitrogen atom, 2-(2,6-$Pr^i_2C_6H_3N{=}CH$)-6-$Bu^tC_6H_3OH$ (L^3H), was used in the study.[71] An analogous synthetic approach allowed the synthesis of the yttrium alkyl complexes $L^3Y(CH_2SiMe_2R)_2(THF)_n$ (R = Me or Ph; n = 1 or 2); however, a mixture of products was obtained in the case of the scandium complex.

Phenols containing the 1,3,5-triazacyclononane fragment as the substituent were used [116] as polydentate ligands in the synthesis of scandium derivatives **83**.

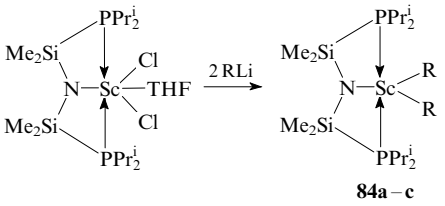


83

$R^1 = CH_2SiMe_3$: R^2 = Me, Pr^i; R^1 = Ph, R^2 = Me.

d. Complexes with monoanionic N,P-containing amide ligands

A series of scandium dialkyl complexes **84a**–**c** containing the amidodiphosphine ligand were synthesised [117] by the exchange reaction of the dichloride $[N(SiMe_2CH_2PPr^i_2)_2]ScCl_2(THF)$ with 2 equivalents of the corresponding alkyllithium reagents. An X-ray diffraction study of compounds **84b**,**c** showed that the complexes are monomeric in the crystalline state and have a distorted trigonal-bipyramidal structure. In the cited study, the reactions of complexes **84** with CO, H_2, CH_3I, nitriles, isocyanides and silanes were investigated; however, all these reactions are accompanied by decomposition of the starting compound and give complex mixtures of products.



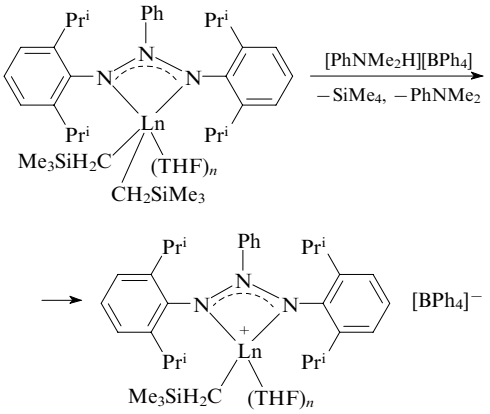
84a–**c**

R = Me (**a**), Et (**b**), CH_2SiMe_3 (**c**).

III. Cationic alkyl complexes

The first cationic rare-earth metal complex containing the substituted alkyl group, $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}.(THF)_n]^+[BPh_4]^-$, was synthesised in 1992.[118] This class of compounds has attracted considerable interest after the discovery [119] of the catalytic activity of cationic scandium complexes in the ethylene polymerisation.

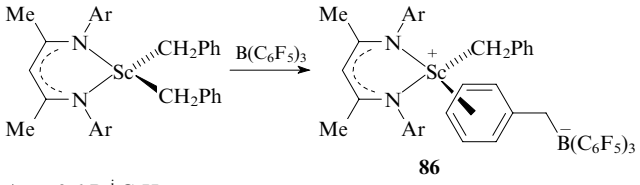
Cationic complexes **85a**–**f** with bulky benzamidinate ligands were synthesised [102, 103] by the reactions of the corresponding dialkyl derivatives with the Brønsted acid $[PhNMe_2H]^+[BPh_4]^-$ in THF. The structures of compounds **85a**–**e** were established by X-ray diffraction.



85a–**f**

Ln = Sc, n = 2 (**a**); Ln = Y, n = 3 (**b**); Ln = La, n = 4 (**c**); Ln = Nd, n = 4 (**d**); Ln = Gd; n = 4 (**e**); Ln = Lu, n = 3 (**f**).

Cationic derivatives can also be prepared by the transfer of one organic ligand, which is coordinated to the metal atom through the M–C σ-bond, to a strong electrophile. For example, the reaction of the scandium dibenzyl complex containing the β-diketiminate ligand with the Lewis acid $B(C_6F_5)_3$ produces cationic compound **86**.[106] Unlike complexes **85a**–**f**, compound **86** exists as a contact ion pair, in which the aromatic ring of the benzyl group is η^6-coordinated to the metal atom.



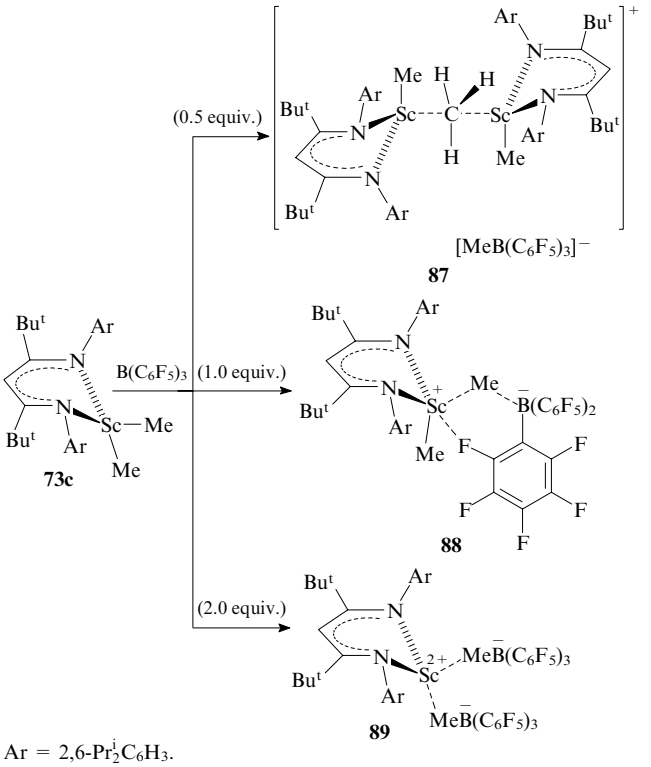
86

Ar = 2,6-$Pr^i_2C_6H_3$.

The reactions of rare-earth metal dialkyl complexes with Lewis acids can produce different cationic complexes depending on the reactant ratio (Scheme 8), as was exemplified [120] by scandium dimethyl complex **73c** containing the β-diketiminate ligand with the bulkier *tert*-butyl substituents at the imine carbon atoms.

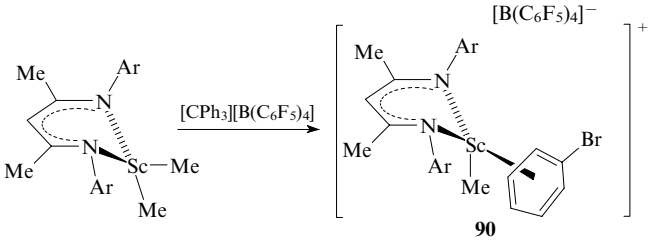
For example, the reaction of **73c** with $B(C_6F_5)_3$ in a molar ratio of 1 : 0.5 affords dinuclear cationic complex **87**, in which two metal atoms are linked by the bridging methyl group. This complex is unstable and decomposes with the evolution of methane. If the reactants are used in a ratio of 1 : 1, the reaction produces monomeric compound **88** existing as an ion pair in which the counterions are linked together by the bridging methyl ligand and by a weak interaction between the scandium atom and the fluorine atom in the *ortho* position of one of the C_6F_5 rings. This compound is stable in the solid state at −30 °C; however, in solution it undergoes decomposition accompanied by the evolution of methane and the metallation of the isopropyl group. ^{1}H NMR spectroscopic studies showed that the ion pair is not dissociated in solution. The treatment of complex **73c** with two equivalents of $B(C_6F_5)_3$ affords doubly charged cationic derivative **89**.

Scheme 8



Ar = 2,6-$Pr^i_2C_6H_3$.

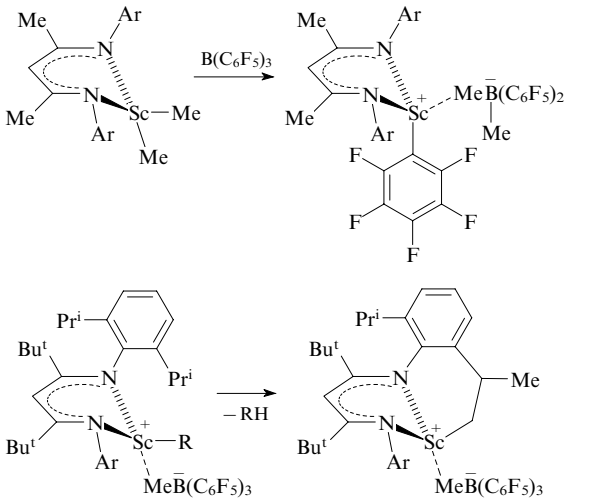
Cationic scandium alkyl complex **90**, which exists as a solvent-separated ion pair and contains the bromobenzene molecule η^6-coordinated to the metal atom in the cationic moiety, was synthesised [121] by the reaction of [ArNC(Me).CHC(Me)NAr]$ScMe_2$ with $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene. In the reactions of complex **90** with arenes having a higher basicity (C_6H_6, C_6H_5Me or $C_6H_3Me_3$) compared to bromobenzene, the arenes replace the PhBr molecule in the metal coordination sphere.



Ar = 2,6-$Pr^i_2C_6H_3$.

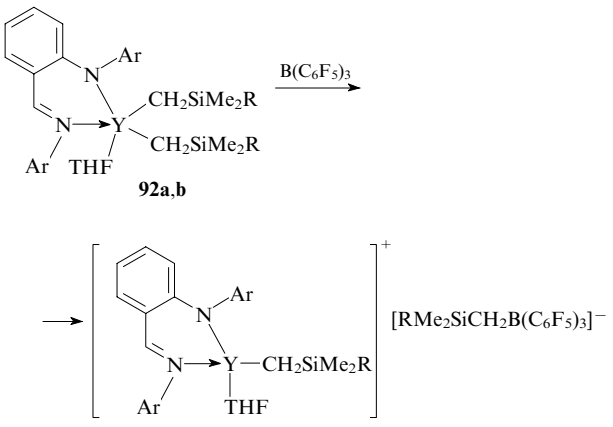
The reactions of the scandium dialkyl complexes $[ArNC(R^1)CHC(R^1)NAr]ScR^2_2$ (R^1 = Me or Bu^t; R^2 = Me, CH_2SiMe_3 or CH_2Bu^t) with $B(C_6F_5)_3$ and $B(C_6F_5)$(BPF) (BPF is perfluorinated biphenyl-2,2′-diyl, $C_{12}F_8$), the properties of the resulting cationic complexes and the dynamics of the constituent contact ion pairs were described.[122] It was found that cationic derivatives of less bulky β-diketiminate ligands containing methyl substituents at the imine carbon atoms are less stable, and the migration of one C_6F_5 group from the boron atom to the metal atom is observed in a toluene solution (Scheme 9). For complexes containing Bu^t-substituted β-diketiminate ligands, this migration is not typical. At room temperature, these compounds are rather stable. However, the metallation of the methyl group of the isopropyl fragment occurs at high temperatures (308–323 K).

Scheme 9



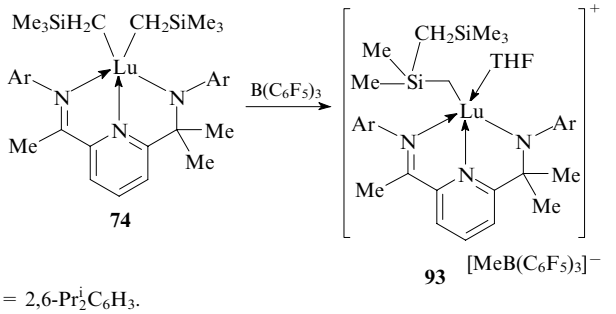
Ar = 2,6-$Pr^i_2C_6H_3$; R = Me, $CH_2SiMe_2CH_2SiMe_3$, $CH_2SiMe_2CH_2$-Bu^t.

Cationic yttrium organometallic derivatives **91** containing the anilido-imine ligand were synthesised as a result of the migration of one CH_2SiMe_2R group (R = Me or Ph) in complexes **92** to $B(C_6F_5)_3$.[104]



Ar = 2,6-$Pr^i_2C_6H_3$; R = Me (**a**), Ph (**b**).

It was demonstrated [110] that the reactions of compounds containing two M–C bonds with Lewis acids can have a more complex mechanism. For example, the reaction of lutetium complex **74** with $B(C_6F_5)_3$ in THF is accompanied by elimination of one methyl group from the $SiMe_3$ fragment to form a new Si–C bond, resulting in the formation of the fragment $CH_2SiMe_2CH_2SiMe_3$ in complex **93**.[110]

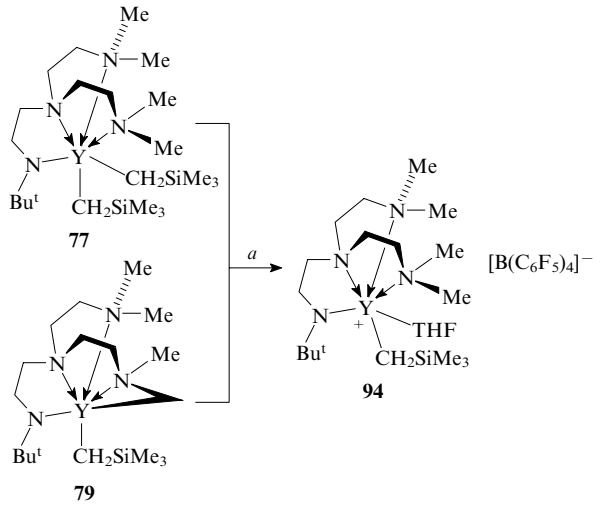


Ar = 2,6-$Pr^i_2C_6H_3$.

The fact that the reaction of $B(C_6F_5)_3$ with complex **80** in THF produces the cationic derivative [(MAC)YCH_2SiMe_3].

.$[B(C_6F_5)_3CH_2SiMe_3]$ was confirmed by multinuclear NMR spectroscopy. This compound is very unstable at room temperature and decomposes within a few minutes to give tetramethylsilane.[115]

It was found [113] that the protonation in the reactions of the Brønsted acid $[PhNMe_2H][B(C_6F_5)_4]$ with complexes **77** and **79** proceeds differently (at the $Y-CH_2SiMe_3$ or $Y-CH_2N$ bond for compounds **77** and **79**, respectively) but gives the same cationic derivative **94**.



(*a*) $[PhNMe_2H][B(C_6H_5)_4]$.

IV. Hydride complexes

Metallocene-type rare-earth metal hydride complexes exhibit unique reactivity [123] and still remain among the most promising catalysts. Most of the known rare-earth metal hydride complexes are dimeric.[3, 123] The only reliably characterised monomeric hydride $[1,3,4\text{-}Bu^t_3C_5H_2]_2CeH$ containing the bulky cyclopentadienyl ligands was described as late as in 2005.[124] Hydride complexes are most often synthesised by the Ln—C σ-bond cleavage with molecular hydrogen [125, 126] or phenylsilane.[127]

The development of post-metallocene chemistry of rare-earth metal hydride complexes has started in recent years. Benzamidinate complex **10**, which was prepared by the hydrogenolysis of compound **2** at 3 atm and 40 °C in benzene (see Scheme 1), was the first and, for many years, the only hydride complex containing no cyclopentadienyl ligands.

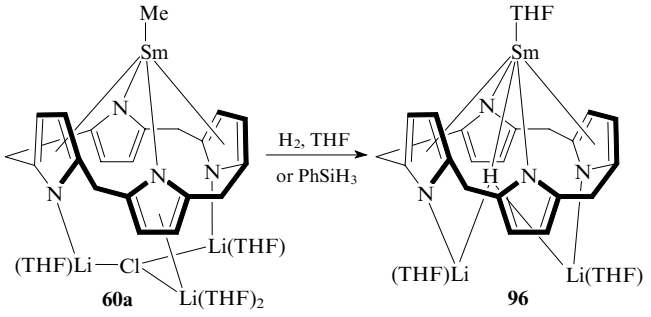
Complex **10** is rather stable in hydrocarbon solvents up to 100 °C; however, it reacts with the C—O bond of THF and also binds to the C—N bonds of acetonitrile and pyridine to form the $[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}N{=}C(H)Me)]_2$ and $[PhC(NSiMe_3)_2]_2Y(py)$ compounds, respectively. The reaction of compound **10** with α-picoline is accompanied by the C—H bond activation to give the $[PhC(NSiMe_3)_2]_2Y(\eta^2\text{-}(C,N)\text{-}2\text{-}CH_2NC_5H_4)$ complex.[26] The reaction of complex **10** with acetylene is accompanied by hydrogen elimination to form dimeric acetylenide $[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}C{\equiv}CH)]_2$. The scandium analogue $[\{PhC(NSiMe_3)_2\}_2Sc(\mu\text{-}H)]_2$ (**11a**) was synthesised [27] by the reaction of the corresponding alkyl complex **11** with H_2 (benzene or hexane, 1 atm, 20 °C). The $[PhC(NSiMe_3)_2]_2ScMe(THF)$ and $[PhC(NSiMe_3)_2]_2ScMes$ compounds react with H_2 to give hydride **11a** only at high temperature (70 °C). Complex **11a** is stable in deuteriobenzene; no evidence of decomposition was observed even upon heating at 60 °C overnight. Compound **11a** is not involved in the exchange reaction with D_2. The dimeric structure of this complex is rather stable, and dissociation was not observed even after the treatment with THF. The addition of complex **11a** at the triple bond of tolane affords the $[PhC(NSi.Me_3)_2]_2ScC(Ph){=}CHPh$ compound.

Lutetium hydride $[\{(Me_3Si)_2NC(NPr^i)_2\}_2Lu(\mu\text{-}H)]_2$ (**95**) stabilised by the guanidinate ligands and containing no coordinated Lewis bases was synthesised [128] by the reaction of the $[(Me_3Si)_2NC(NPr^i)_2]_2LuCH_2SiMe_3$ complex with $PhSiH_3$ (in a ratio of 1 : 1) in hexane. This compound differs from other bis(guanidinate)-type derivatives by the asymmetric coordination of the guanidinate ligands in two $[(Me_3Si)_2NC(NPr^i)_2]_2Lu$ fragments.

Yttrium alkyl complexes **17a**,**b** readily react with phenylsilane in benzene at room temperature to form hydride **18**. This hydride can also be prepared by the hydrogenolysis of compounds **17a**,**b** under high pressure at room temperature in deuterobenzene. The exchange of the hydride ligands for deuterium from the solvent was observed upon storage of hydride **18** in THF-d_8. In THF, complex **18** binds to the C=C bonds of ethylene and hex-1-ene to give the corresponding alkyl complexes (see Scheme 2).

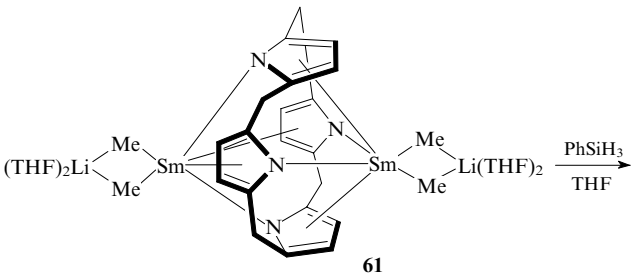
It was reported [37] that the hydrogenolysis of the $[2,6\text{-}Pr^i_2C_6H_3N(CH_2)_2NC_6H_3Pr^i_2\text{-}2,6]YCH(SiMe_3)_2(THF)$ complex in toluene under an H_2 pressure of 1.5 atm proceeds very slowly. The hydrogenation of the Y—C bonds was accompanied by the insertion of H_2 at one of the two Y—N bonds of two diamide ligands to form the trinuclear $[Y_3\{2,6\text{-}Pr^i_2C_6H_3NH(CH_2)_2NC_6H_3Pr^i_2\text{-}2,6\}_2\{2,6\text{-}Pr^i_2C_6H_3N(CH_2)_2N.C_6H_3Pr^i_2\text{-}2,6\}(\mu\text{-}H)_3(\mu_3\text{-}H)_2(THF)]$ complex.

The μ_3-bridging coordination of the hydride ligand linking together the samarium atom and two lithium atoms was observed [82] also in hydride complex **96** containing the calix-pyrrole ligand. Complex **96** can be synthesised from methyl derivative **60a** by either the hydrogenolysis in THF at room temperature or the treatment with phenylsilane.

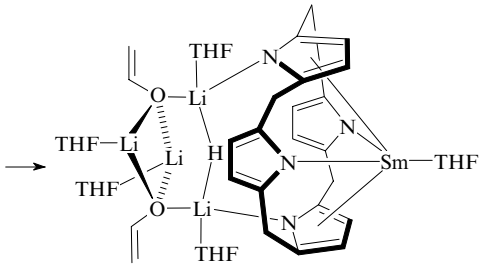


The Sm—H distance in complex **96** is 2.25(7) Å, which is substantially larger than the bond lengths in known dimeric metallocene-type samarium hydrides (2.05 Å).[129] Complex **96** is stable in THF at room temperature for several weeks or at 60 °C for several hours. Compound **96** rapidly reacts with ethylene at room temperature and under atmospheric pressure to form the vinyl derivative accompanied by hydrogen elimination.

Heterobimetallic five-coordinate hydride complex **97** was prepared in 10% yield by the treatment of samarium methyl complex **61** with phenylsilane in THF at room temperature. The structure of complex **97** was established by X-ray diffraction. The complex contains two $LiOCH{=}CH_2$ fragments, which are formed, apparently, as a result of the cleavage of the THF molecule under the action of two MeLi molecules.[83] The second hydride-containing product, $(Et_8\text{-calix-pyrrole}).Sm(H)Li_2(THF)_6$, was also isolated from the reaction mixture; however, the latter product was not reliably characterised.

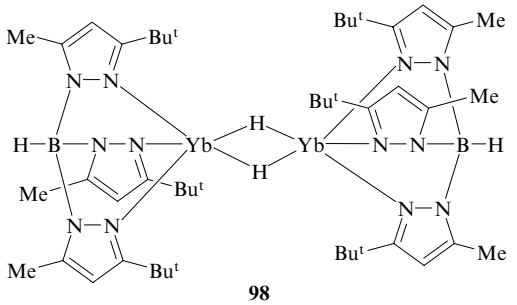


61



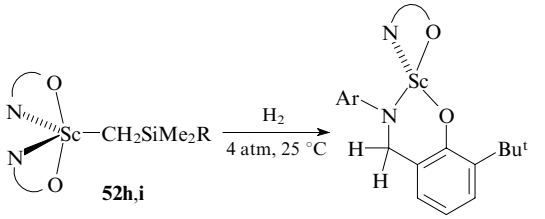
97

The only hydride complex of lanthanides in the oxidation state +2 (compound **98**) was described. This complex was synthesised [130] with the use of the tris(pyrazolyl)borate ligands (TPB-Me,Bu^t) as the stabilising coordination environment.

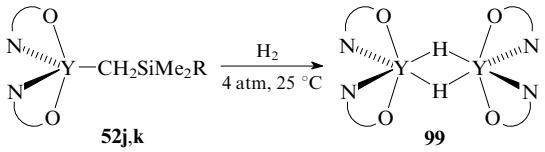


98

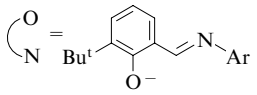
The hydrogenolysis of alkyl complexes **52h**–**k** stabilised by the salicylaldiminate ligands L was found [69, 71] to proceed differently depending on the nature of the metal. For example, the hydride compound that is formed in the case of scandium immediately binds to the C=N bond of one of the ligands L, whereas dimeric hydride **99** was isolated in the case of yttrium. The latter complex is inert to ethylene.



52h,**i**



52j,**k** **99**

R = Me, Ph;  ; Ar = 2,6-Pr$^i_2$C$_6$H$_3$.

The reaction of complex **34** with hydrogen was demonstrated to produce centrosymmetric dimeric hydride $[\{Me_2Si(NBu^t)(OBu^t)\}_2Y(\mu\text{-}H)]_2$, which was detected [50] in the reaction mixture by ^{1}H NMR spectroscopy. However, attempts to isolate the hydride complex failed because this complex undergoes disproportionation in solution to give the $[Me_2Si(NBu^t)(OBu^t)]_3Y$ compound.

The reactions of complexes **84b**,**c** with hydrogen are accompanied by elimination of the corresponding alkanes; however, hydrides were not detected in the reaction mixtures, and the ^{31}P NMR spectra provided evidence for the presence of a complex mixture of products.[117]

An attempt to synthesise the yttrium dihydride complex by the reaction of the dimethyl derivative (TPB-Me$_2$)YMe$_2$(THF) with H_2 under a pressure of 8 atm at 0 °C led to the formation of a thermally unstable complex, which was characterised by IR spectroscopy.[114]

V. Non-metallocene rare-earth organometallic derivatives in catalysis of transformations of unsaturated substrates

1. Catalysis of alkene and diene polymerisation

Yttrium dihydride complex **10** catalyses the ethylene polymerisation under a pressure of 4 atm at 65 °C in deuteriobenzene.[25, 26] An increase in the monomer pressure to 70 atm improves of the efficiency of the reaction, but the activity, on the whole, remains low [4 (g PE) (mmol catalyst)$^{-1}$ h^{-1}]. The resulting polyethylene has a molecular mass $M_w = 2.399 \times 10^5$, $M_n = 4.63 \times 10^4$ and a high polydispersity ($M_w/M_n = 5.2$). It should be noted that no yttrium organometallic derivatives, except for complex **10**, were detected in the reaction mixture by ^{1}H NMR spectroscopy. Yttrium benzyl complex **1** also initiates the ethylene polymerisation, but the activity of this complex is even lower than that of hydride **10**. Both complexes do not catalyse the propylene and hex-1-ene polymerisation. No traces of oligomerisation products or allyl complexes were found even at 80 °C. Scandium analogue **11a** proved to be [27] virtually inactive in the ethylene and propylene polymerisation.

Yttrium dialkyl complex **68a** with the bulky amidinate ligand initiates the ethylene polymerisation in the presence of the activator $[PhNMe_2H][B(C_6F_5)_4]$ at 50 °C and a monomer pressure of 5 atm at a high rate.[102] After a polymerisation time of 5 min, the molecular mass M_w of the polymer was 4.3×10^5; after 30 min, M_w was 1.211×10^6, the polydispersity being very low ($M_w/M_n = 1.2$). Calculations demonstrated that there is one yttrium centre per 1.1 polymer chain in the course of polymerisation, which is indicative of the living polymerisation and a low probability of the chain transfer through β-elimination. It was noted that the efficiency of the catalyst decreases with time. The catalyst efficiency was 1037 (kg PE) mol^{-1} h^{-1} atm^{-1} at a reaction time of 5 min, and it was only 400 (kg PE) mol^{-1} h^{-1} atm^{-1} after 30 min. It should be noted that the six-coordinate analogue of compound **68a** containing an additional THF molecule in the metal coordination sphere is absolutely inactive in the ethylene polymerisation under analogous conditions. However, the addition of partially hydrogenated $AlBu^i_3$ (TIBAO) to a mixture of compound **68a** and $[PhNMe_2H][B(C_6F_5)_4]$ resuts in the formation of catalytic systems active in the ethylene polymerisation [the efficiency is 2670 (kg PE) mol^{-1} h^{-1} atm^{-1}, $M_w/M_n = 2.1$]. In the presence of TIBAO, M_w of the polymer is somewhat lower and the polydispersity is higher (~2) than the corresponding characteristics in the absence of this additive.

The catalytic activity of dialkyl amidinate complexes **68b**–**f** in the ethylene polymerisation in the presence of $[PhNMe_2H][B(C_6F_5)_4]$ and TIBAO at 30 °C and a monomer pressure of 5 atm was investigated.[103] It was found that the catalytic activity of the systems substantially depends on the ionic radius of the metal atom. Scandium having the smallest

ionic radius among the rare-earth elements, as does lanthanum having the largest ionic radius, show low activities. The activities of about 3000 (kg PE) mol^{-1} h^{-1} atm^{-1} were observed for metals having intermediate ionic radii (Y and Gd). The polyethylene prepared in the presence of these catalysts is characterised by a high molecular mass ($M_w = 1.5 \times 10^6$) and the polydispersity $M_w/M_n \approx 2$. The conclusion was drawn that the main mechanism of the chain transfer in this system involves the transfer of the alkyl radical to the Al atom. It should be noted that the lutetium complex having a small ionic radius showed a moderate activity [342 (kg PE) mol^{-1} h^{-1} atm^{-1}] and gave rise to the product with a low polydispersity ($M_w/M_n = 1.4$), which is indicative of the absence of the chain transfer, as opposed to systems with complexes of metals with larger ionic radii.

Lutetium hydride **95** stabilised by guanidinate ligands catalyses [128] the ethylene polymerisation; however, its efficiency is low. Complex **95** belongs to a few rare-earth metal derivatives initiating the propylene polymerisation [the activity was 3.9 (kg PE) mol^{-1} h^{-1} atm^{-1}]. Compound **95** is also efficient in the styrene polymerisation at room temperature and allows the preparation of polymers with a high molecular mass $M_w = 1.25 \times 10^6$ and a rather low polydispersity $M_w/M_n = 1.54$.

Heterobimetallic bis(guanidinato)alkyl complexes **59b**,**c** initiate the styrene polymerisation [79] in the temperature range of 70–100 °C. It should be noted that the reaction does not proceed at 55 °C; at 100 °C, the yield of the polymer is substantially lower, which was accounted for by the deactivation of the catalysts at high temperatures. The polystyrene samples have molecular masses in a range of $(1.72-5.89) \times 10^4$ and rather low polydispersities (~ 2), which increase with temperature. Studies of the microstructures of the resulting polymer samples showed that they are predominantly atactic. However, the macromolecules contain from 53% (70 °C) to 28% (85 °C) of syndiotactic fragments depending on the polymerisation temperature.

In spite of numerous investigations on the synthesis of rare-earth metal complexes with β-diketiminate ligands, data on their catalytic activity are scarce. Scandium dimethyl complex **73c** showed high catalytic activity in the ethylene polymerisation [300–1200 (kg PE) mol^{-1} h^{-1} atm^{-1}] in the presence of $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ as the activator and poly-(methylalumoxane) (MAO) as the cocatalyst at 50 °C.[120] This complex allows the preparation of polyethylene with a high molecular mass [$(0.851-1.866) \times 10^6$] and a rather narrow molecular mass distribution (MMD) ($M_w/M_n = 1.7-2.2$). The use of an analogous complex containing Cl ligands instead of Me groups in the presence of MAO leads to a decrease in the catalytic activity of the system to 9.9×10^4 (kg PE) mol^{-1} h^{-1} atm^{-1} (polyethylene has $M_w = 1.357 \times 10^6$, $M_w/M_n = 2.2$).

Yttrium alkyl and hydride complexes **17a**,**b** and **18** containing the dianionic ligand DADMB proved to be poorly active in the ethylene polymerisation.[35]

A study of yttrium dialkyl complexes stabilised by the monoanionic tetradentate N-donor ligands (L) in the ethylene polymerisation showed [111] that the nature of the ligand has a decisive effect on the catalytic activity of the complexes generated in the $LY(CH_2SiMe_3)_2$–$[PhNMe_2H][B(C_6F_5)_4]$ systems. For example, complexes **75a**,**b** containing the 1,4,7-triazacyclononane ligand proved [111] to be active catalysts for the ethylene polymerisation in the presence of $[PhNMe_2H][B(C_6F_5)_4]$ (toluene, 30–80 °C, 5 atm). Their efficiency was $(0.70-1.79) \times 10^3$ (kg PE) mol^{-1} h^{-1} atm^{-1}. The polyethylene samples had a high polydispersity ($M_w/M_n = 4.0-6.0$). In addition, catalysts lost 5%–30% of the initial activity during a rather short period of time (10–15 min). Unlike complexes **75a**,**b**, compound **77**, in which the yttrium atom is in an analogous coordination environment but which contains the structurally different N,N-donor ligand, is inert to ethylene in the presence of $[PhNMe_2H][B(C_6F_5)_4]$ as the activator. In the presence of $[Ph_3C][B(C_6F_5)_4]$ as the activator, which does not form the free Lewis base $PhNMe_2$ in the reactions with dialkyl complexes, complex **77** catalyses the ethylene polymerisation (toluene, 50 °C, 5 atm) but it loses catalytic activity during 4 min.[113]

Yttrium dialkyl and diaryl complexes containing the dimethyl tris(pyrazolyl)borate ligands (TPB-Me_2) or (TPB-Me_2)YR_2(THF) (R = Me, Bu^t, CH_2SiMe_3 or Ph) catalyse the ethylene polymerisation giving a linear polymer with a high molecular mass (up to 2×10^6) and a high polydispersity (2.50–4.14).[114] The complex with R = Bu^t proved to be more active (the total turnover number was 1932).

Yttrium dialkyl complex **81** initiates the ethylene polymerisation but it is inert to propylene and butadiene.[87]

The treatment of neodymium alkoxide $Nd_3(\mu_3\text{-}OBu^t)_2.(\mu_2\text{-}OBu^t)_3(OBu^t)_4(THF)_2$ (Refs 62 and 131) with dialkylmagnesium compounds affords systems, which can catalyse the ethylene polymerisation. The polymerisation at 0 °C and a monomer pressure of 1 atm in the presence of these catalysts and phenylsilane or H_2 gives low-molecular-mass polyolefins [the activity is 5–20 (kg PE) mol^{-1} h^{-1} atm^{-1}].[131]

Complexes **32a**,**b**,[49] **35** (Ref. 52) and **54** (Ref. 73) proved to be inactive as initiators for the ethylene polymerisation.

The heterobimetallic diiminopyridine complex [2,6-{2,6-$Pr^i_2C_6H_3NC(=CH_2)\}_2C_5H_3N$]Nd(μ-Me)(μ-Cl)[Li(THF)$_2$] containing the bridging methyl and chloride ligands, which link together the neodymium and lithium atoms, proved to be a highly efficient catalyst for the synthesis of *cis*-polybutadiene, whereas the activity of the fully methylated analogue (containing the Me group instead of the Cl atom) was unexpectedly much lower.[39]

The catalytic system, which was prepared by the treatment of neodymium alkoxide $Nd_3(OBu^t)_9(THF)_2$ with dialkylmagnesium reagents, proved to be inefficient in the butadiene polymerisation, whereas systems based on tris(phenoxides) $Nd(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)_n$ ($n = 0$ or 1) are suitable for the living polymerisation of butadiene and the preparation of polymers with a low polydispersity ($M_w/M_n = 1.3$) containing up to 95% of *trans* units.[132] These systems allow also the synthesis of butadiene–styrene copolymers with a molecular mass M_n up to 5×10^4 and a styrene content of 3%–15%.

2. Catalysis of polymerisation of polar monomers

a. Acrylic monomers

Yttrium and samarium alkyl complexes **13** and **14a**,**b** were studied [32] as initiators for the methyl methacrylate (MMA) polymerisation. Compounds **13** and **14a** exhibit high catalytic activity and isospecificity in both the block and solution polymerisation of MMA. Compound **14a** showed good results as regards the stereoregularity of polymer products in a wide temperature range (from −40 to +65 °C); however, the isotacticity of poly(methyl methacrylate) (PMMA) samples somewhat decreases with temperature. The block copolymerisation initiated by complex **14a** affords a isotactic polymer with a very high molecular mass ($M_n = 1.41 \times 10^6$) and a low polydispersity ($M_w/M_n = 1.31$). Yttrium complex **13** provided much lower selectivity but the molecular mass distribution remained rather narrow (1.24–1.98). It should be noted that methyl complex **14b** appeared to be absolutely inactive in the MMA polymerisation.

The scandium complex (BDPPpyr)$ScCH_2SiMe_3$(THF) with the tridentate diamino-substituted pyridine ligand (see Section II.1.b) catalyses [38] the MMA polymerisation at 40 °C in toluene at a high rate to give PMMA with molecular masses $M_w = 1.29 \times 10^5$ $M_n = 8.1 \times 10^4$ and a low polydispersity ($M_w/M_n = 1.6$). Analogous yttrium and lutetium complexes

with large ionic radii exhibited very low activity, whereas derivatives of other ligands examined in the study [38] proved to be inactive.

Heterobimetallic neodymium and ytterbium complexes **58a**,**b** initiate the MMA polymerisation [78] at good rates even at −78 °C. The PMMA samples have predominantly syndiotactic structures, high molecular masses ($>10^4$) and polydispersities varying from 1.61 to 1.93.

Neodymium bis(guanidinate) complex **59b** proved to be an efficient catalyst for the MMA polymerisation at 40 °C. The resulting polymer [80] had a molecular mass of 10.8×10^4 and a polydispersity of 2.16.

The use of the $Nd_3(\mu_3\text{-}OBu^t)(\mu_2\text{-}OBu^t)_3(OBu^t)_4.(THF)_2$ – $(n\text{-}C_6H_{13})_2Mg$ systems allows the synthesis of polyethylene–PMMA block-copolymers.[131] The $Nd(OC_6H_2.Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)$ and $Nd(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_3$ – $(n\text{-}C_6H_{13})_2Mg$ systems [132] catalyse copolymerisation of butadiene with glycidyl methacrylate, resulting in the formation of block polymers.

b. ε-Caprolactone and lactides

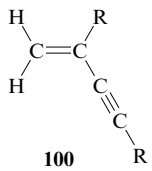
Bis(guanidinate) complexes **59b**,**c** are efficient catalysts for the ε-caprolactone polymerisation.[80] In the case of neodymium complex **59b**, the conversion achieved 100% at 20 °C during 15 min even at the monomer : initiator ratio of 1000 : 1; ytterbium derivative **59c** proved to be somewhat less active. The resulting polymer has a high molecular mass [$M_n = (7.44-11.03)\times10^4$] but a rather wide MMD ($M_w/M_n = 1.92-2.96$).

Yttrium alkyl complexes **66** and **81** and lutetium alkyl complex **67** containing the phenoxide ligands were demonstrated [87] to initiate ε-caprolactone polymerisation. However, data on the activity of the catalysts and the properties of the polymers were not reported.

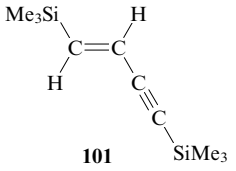
The use of scandium complex **82a** with the phenoxy-imine ligand allows the polymerisation of ε-caprolactone with a quantitative conversion at 0°C during 1 min. The molecular mass of the polymer was 7.1×10^4, and the polydispersity was 2.9.[72] Complex **56b** exhibited somewhat lower activity;[75] however, the resulting polyester had a much lower polydispersity ($M_w/M_n = 1.49$) and a lower molecular mass ($M_n = 5.05\times10^4$). Related bis(phenoxide) complex **54** initiates the living polymerisation of racemic lactide at a high rate, which gives predominantly a heterotactic polymer.[133]

3. Catalytic C−C bond formation (dimerisation of alkynes)

An investigation of the catalytic activity of yttrium complexes **1**, **2** and **10** in the dimerisation of terminal alkynes showed [26] that, as opposed to systems with metallocene-type catalysts, [134, 135] the reaction pathway in the presence of these complexes substantially depends on the size of the substituent at the triple bond of the substrate. For example, dimerisation of alkynes RC≡CH with small substituents (R = H, Me or Pr^i) was not observed even upon prolonged heating (80 °C), whereas alkynes with bulky substituents (R = Ph, $SiMe_3$ or Bu^t) do undergo dimerisation under analogous conditions. It should be noted that the rate of alkyne dimerisation catalysed by amidinate complexes **1**, **2** and **10** is much lower than that in the presence of bis(cyclopentadienyl)-type complexes.[134] The regioselectivity of the reaction depends also on the nature of alkyne. Thus, the PhC≡CH and $Bu^tC\equiv CH$ compounds undergo the selective head-to-tail dimerisation to form 2,4-disubstituted but-1-en-3-ynes **100**, whereas the reverse selectivity is observed for $Me_3SiC\equiv CH$, and the reaction affords exclusively the 1,4-substituted head-to-head addition product, *viz*., *trans*-$Me_3SiC(H)=C(H)C\equiv CSiMe_3$ (**101**).



100



101

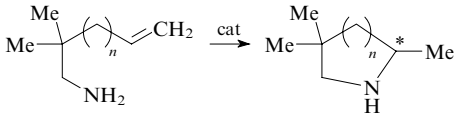
R = Bu^t, Ph.

The cationic complex $[LLa(CH_2SiMe_3)]^+[B(C_6F_5)_4]^-$, which was prepared by the reaction of $[PhNMe_2H][B(C_6F_5)_4]$ with the $LLa(CH_2SiMe_3)_2$ complex (**75c**), was used *in situ* in the catalysis of the phenylacetylene dimerisation. At 50 °C, the reaction proceeds at a high rate and a very high selectivity to give *cis*-1,4-diphenylbut-1-en-3-yne in 99% yield.[112]

4. Catalytic C−N bond formation (hydroamination of alkenes)

The catalytic hydroamination of alkenes and alkynes resulting in the addition of amines at multiple bonds of unsaturated substrates is a very convenient, efficient and environmentally safe procedure for the synthesis of nitrogen-containing compounds.[14, 136, 137] Organic rare-earth metal derivatives are among the most promising catalysts for the hydroamination–cyclisation of unsaturated compounds with unactivated double bonds proceeding under mild conditions at a high rate and a high enantioselectivity, which allows the synthesis of nitrogen-containing heterocyclic, including biologically active, compounds.[15, 16]

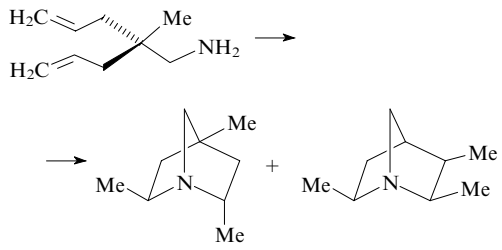
Lanthanum alkyl complexes **48** and **49** containing the chiral Biphen ligand proved to be efficient catalysts for the hydroamination–cyclisation of 2,2′-dimethylpent-4-enylamine and hex-5-enylamine at room temperature, the activity of monomeric complex **49** being almost twice as high as that of dimer **48**.[66]



n = 1, 2.

Unfortunately, the enantioselectivity of complexes **48** and **49** is low, and the reactions produce racemic mixtures of heterocycles. The use of the Binol-$SiAr_3$ ligands with the bulky Ar_3Si substituents at positions 3 and 3′ (complexes **50** and **51**) allows not only the retention of high activity in the hydroamination, but also a substantial enhancement of the enantioselectivity of the reaction (to 95%).[67, 68] In the presence of these complexes, the cyclisation of aminopentenes proceeds at a high rate even at room temperature, whereas the reaction of aminohexenes requires high temperature (60–100 °C). The catalytic activity of these complexes increases with increasing ionic radius of metal. Compound **51** catalyses the hydroamination of styrene with propylamine at 60 °C, the addition being anti-Markovnikov.[68]

Yttrium complexes **28a**–**c** also exhibited high activity in the catalysis of the hydroamination–cyclisation of various aminoalkenes and aminoalkynes.[43] The electron-withdrawing effect of the dichlorophenyl substituents (compound **28c**) enhances the stability of the catalyst to degradation as a result of protonolysis, which is manifested in its high activity in the cyclisation of pent-4-enylamine and 5-phenylpent-4-ynylamine. The double cyclisation of 2-allyl-2-methylpent-4-enylamine can be performed at 60 °C with the use of complexes **28a** and **28c**; this reaction affords 2,4,6-trimethyl-1-azabicyclo[2.2.1]heptane as a mixture of *endo*,*endo* and *exo*,*exo* isomers.



The use of scandium organometallic complexes with salicylaldiminate and β-ketiminate ligands for the initiation of the hydroamination–cyclisation of aminoalkynes and aminoalkenes was documented.[138] In the cited study, the first cationic system (compound **88**) initiating the intramolecular hydroamination was described.

Complexes **52i**, **73c** and **52l** (L = Sn, Ar = Mes, R = Ph) catalyse the hydroamination–cyclisation of 5-phenylpent-4-ynylamine (25 °C for complexes **52i**,**l** and 65 °C for complex **73c**) giving substituted pyrroline in quantitative yield. However, these complexes are inactive in the catalysis of the intermolecular hydroamination of hex-1-yne with aliphatic amines. Complex **52i** containing ligands with the bulky diisopropylphenyl substituent at the imine nitrogen atom is inactive in the hydroamination of 2,2-diphenylpent-4-enylamine. However, the use of a less bulky ligand containing the mesityl substituent (complex **52l**) results in the appearance of the catalytic activity; the complete conversion is achieved at 65 °C for 2 h. β-Diketiminate complex **73c** catalyses the hydroamination of 2,2-diphenylpent-4-enylamine at room temperature but at a low rate. The activity of the catalyst was increased by a factor of ~60 and the amount of the catalyst charge was halved with the use of cationic derivative **88**. The use of this cationic complex makes it also possible to perform the cyclisation of aminohexenes, which is, as a rule, a more complex process compared to aminopentenes.

5. Catalytic C–Si bond formation (hydrosilylation of alkenes)

Yttrium methyl and hydride complexes **17a** and **18** can catalyse the formation of ethylphenylsilane from ethylene and $PhSiH_3$ at room temperature and an ethylene pressure of 0.35 atm.[139] The hydrosilylation of hex-1-ene, styrene and norbornene with $PhSiH_3$ proceeds in the presence of complex **17a**, whereas cyclohexene, α-methylstyrene and *trans*-stilbene are not involved in this reaction. In the presence of this complex, secondary silane $PhMeSiH_2$ is involved in the addition reaction only with hex-1-ene and styrene. It should be noted that aliphatic alkenes give predominantly anti-Markovnikov addition products, whereas the hydrosilylation of styrene affords benzylsilane derivatives as the major products. Complex **17a** containing the enantiomerically pure (*S*)-biphenyl ligand showed a high enantioselectivity in the catalysis of the hydrosilylation of norbornene with phenylsilane (*ee* 90.4%).

Lanthanum complexes **48** and **49** (Ref. 66) catalyse the hydrosilylation of hex-1-ene, styrene and norbornene with ethylphenylsilane at 60 °C, the catalytic activity of monomeric complex **49** is, as a rule, lower than the activity of dimeric complex **48** containing no coordinated THF molecules. The hydrosilylation of styrene proceeds at a high rate and a high selectivity to give predominantly the Markovnikov addition product. Unexpectedly, the rates of hydrosilylation of hex-1-ene and norbornene appeared to be substantially lower than that of styrene. Both reactions are stereoselective and give exclusively the 1,2-addition product and the *exo* adduct for hex-1-ene and norbornene, respectively.

6. Catalytic C–B bond formation (hydroboration of alkenes)

Yttrium bis(amidinate) complexes **1**, **2** and **10** (Refs 12 and 26) catalyse the hydroboration of hex-1-ene with catecholborane. However, the activity of these complexes is substantially lower than that of the $(\eta^5\text{-}C_5Me_5)_2LaCH(SiMe_3)_2$ complex.[13] In all reactions, the catalyst deactivation was observed, which is apparently due to the reaction of catecholborane with the benzamidinate ligands. The catalytic activity of complexes **1**, **2** and **10** is substantially higher than that of metallocene-type yttrium catalysts.

* * *

The data summarised in the present review clearly show that the last decade witnessed considerable advances in the search for new ligand systems alternative to the cyclopentadienyl ligand and capable of stabilising highly reactive rare-earth organometallic derivatives. The progress achieved in this field confirms great possibilities for manipulatiing the reactivity of rare-earth metal complexes containing M–C and M–H bonds by the design of ligand systems and the coordination sphere of the central atom and a considerable potential of these compounds in the catalysis of various transformations of unsaturated substrates. The further progress in the catalytic applications of rare-earth organometallic compounds would be expected to be determined by advances in the chemistry of their hydride and cationic complexes.

This review has been written with the financial support of the Russian Foundation for Basic Research (Project No. 05-03-32390), the Russian Science Support Foundation and the Federal Agency for Science and Innovations of the Russian Federation (Contract No. 02.513.11.3029).

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