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Organolanthoid Chemistry: Synthesis, Structure, Catalysis

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With contributions by
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W. A. Herrmann

With 113 Figures and 47 Tables

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Rare-Earth Metals: Coordination Chemistry of the Periodic Table's "Footnotes"

Horizons in Synthesis · Habit of Structures · Patterns of Reactivity

> "*Lanthanons ...*
>
> *These elements perplex us in our rearches* [*sic*!], *baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us — mocking, mystifying and murmuring strange relevations and possibilities.*"
>
> Sir William Crookes (February 16, 1887)

Preface

The rare-earth elements — first row of fourteen "footnotes" in the periodic table — have long been strongly neglected in organometallic chemistry. It was only in the eighties that a number of research laboratories began to focus on the lanthanides and their close relatives — scandium and yttrium —, at a time when selected members of this group of elements were well-established in a huge number of applications. In particular, the field of "high-tech materials" is dependent on rare-earth components to a significant extent: they tune magnetic/electrical properties of metallic and oxidic materials, optical properties for colour television and electric lighting, mechanical properties of hard materials (metal oxides and nitrides), and the performance of catalysts in mineral oil cracking, olefin polymerization, methanol synthesis, Fischer–Tropsch synthesis and exhaust gas chemistry (e.g., lambda sensors). An annual increase of more than 15% in high-tech applications of lanthanides is expected in the near future. As a matter of fact, these broad-scope applications initiated the recent intense research into the coordination and organic chemistry of the rare-earth elements.

For example, volatile molecular precursor compounds are a primary goal of CVD (chemical vapor deposition) techniques for generating thin films of oxidic, nitridic, and carbidic lanthanide coatings on top of other (mostly inorganic) materials. Other activities are aimed at the improvement of catalysts on the molecular level: certain organolanthanide compounds were found to exhibit specific catalytic properties in reactions that are otherwise difficult to perform, e.g. cyclohydroamination of olefins, polymerization of olefins, and polycondensation of lactides to make biodegradable polymers (Lewis-acid catalysis). The even simpler compound samarium(II) iodide, generated from a Grignard-type reaction of 1,2-diiodoethane and metallic samarium ($Sm + ICH_2CH_2I \rightarrow SmI_2 + CH_2{=}CH_2$; H.B. Kagan), effects a clean reductive coupling of keto compounds to vicinal diols.

A more differentiated coordination chemistry of this and related lanthanide elements seems necessary to eventually conduct these reactions catalytically instead of stoichiometrically. This is clearly one of the major challenges in the ongoing organolanthanide research. At present, the entire field of catalysis involving the Periodic Table's "footnotes" is largely underdeveloped. This is not so much due to the normally pronounced hygroscopicity of lanthanide compounds (with this property in the first place resulting from the Lewis acidity of Ln-ions and their "oxophilicity"), but more a result of insufficient *synthesis* research. It is a known fact that increasing knowledge on the synthetic methodology of a given group of elements or a particular class of compounds pushes their applications by virtue of an improved understanding of *reactivity* and *structure.*

To keep up with the rapid development in the molecular (coordination) chemistry of the rare-earth metals, a special volume of *Topics in Current Chemistry* was recognized as the ideal forum for up-to-date essays on basic compounds, their syntheses, structures and reactivities. As guest editor, I am proud to present a small but outstanding collection of contributions from the forefront of this field: *Reiner Anwander*, a former Ph.D. student of mine (Technische Universität München, 1992) and later a post-doctoral fellow of Bill Evans in Irvine/USA, has furnished two articles on "*Lanthanide Amides*" and "*Routes to Monomeric Lanthanide Alkoxides*", both built up on a complete list of literature references up to mid-1995. *Frank Edelmann*, now a professor of inorganic chemistry at Magdeburg University, has written updated reviews on "*Lanthanide Metallocenes in Homogeneous Catalysis*" and "*Rare Earth Complexes with Heteroallylic Ligands*". Both these authors reveal thorough experimental experience regarding the topics of their contributions. A "feature article" by *Reiner Anwander* and myself attempts to focus on the lanthanoids' principles regarding structure and reactivity. It is to be hoped for that the present volume will further draw the attention of our scientific community to the virtuosity of lanthanide molecular chemistry. It is the plethora of lanthanide compounds, structures, and reactivities that will soon raise these "footnotes" into the main text of chemistry.

München, April 1996 Wolfgang A. Herrmann

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Small Ring Compounds in Organic Synthesis V

Features of Organolanthanide Complexes

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Reiner Anwander and Wolfgang A. Herrmann

The intrinsic properties of the lanthanide elements guarantee promising applications in the fields of catalysis and material science. How to cope with these features on a molecular level and under anaerobic conditions is discussed, including thermodynamic and kinetic considerations. Due to the importance of a prolific metal/ligand synergism, current developments in ligand design are emphasized.

List of Symbols and Abbreviations

BINOL	binaphthol
CN	coordination number
Cp	η^5-cyclopentadienyl
DME	1,2-dimethoxyethane
Diglyme	di-β-methoxyethylether
E	element
hfc	3-(heptafluoropropylhydroxymethylene)-*d*-camphorato
HSAB	hard soft acid base
Im	imidazole
L	ligand
Ln	lanthanide (Sc, Y, La, Ce–Lu)
MOCVD	metal-organic chemical vapor deposition
Py	pyridine
TBP	tri-*n*-butylphosphane
Tf	"triflate" ligand, CF_3SO_3
thd	2,2,6,6-tetramethyl-3,5-heptandionate
THF	tetrahydrofurane
TMEDA	tetramethylethylenediamine
tritox	tri-*tert*-butyl methoxide
Z	nuclear charge

1 Introduction

The terms '*contraction*' and '*separation*' have probably been most commonly associated with the lanthanide elements and students are certainly confronted with precisely these key words in textbooks and lectures. However, the modern synthetic chemist has to consider numerous intrinsic factors, especially when it comes to the synthesis of well-defined molecular species with potential relevance to the catalysis and the material sciences. As a rule, most review articles covering organolanthanide chemistry point out the background which determines structural behavior and reactivity patterns. The last 20 years have witnessed a rapid development in organolanthanide chemistry, and this has been recorded in several books [1] and numerous review articles. A collection of the latter dealing with principles of synthesis, properties and methods of characterization is presented in Tables 1 and 2, classified according to the prevailing Ln-X(C, N, O) fragment [2–56]. The chemistry based on lanthanide carbon bonds, in particular cyclopentadienyl chemistry, still dominates this scenario and the fact that research is becoming more and more specialized is tendentiously reflected in the titles of the topics reviewed. Table 3 considers promising applications in this field. Macrocyclic ligands exhibiting Ln-N and Ln-O bonds are not considered in this survey [57]. Review articles which are addressed to more fundamental problems, such as aspects of bonding and spectroscopy, are mentioned in the particular subsection.

Table 1. Review articles covering predominantly Ln–C based organolanthanide chemistry[a]

Author(s)	Topic	Year	Ref.
Gysling H, Tsutsui M	Cyclopentadienyls of Ln(III) and Ln(II)	1970	[2]
Tsutsui et al	σ-Bonded derivatives	1976	[3]
Marks TJ	Chemistry and spectroscopy	1978	[4]
Lappert MF, Singh A	Bis(cyclopentadienyl) chlorides	1982	[5]
Marks TJ, Ernst RD	Comprehensive general overview	1982	[6]
Forsberg JH, Moeller T	General overview	1983	[7]
Thompson ME, Bercaw JE	Alkyl and hydride derivatives of permethylscandocene	1984	[8]
Schumann H et al.	General overview	1984	[9]
Evans WJ	General overview	1985	[10]
Bochkarev MN et al.	General overview	1985	[11]
Evans WJ	Low oxidation states	1987	[12]
Beletskaya IP et al.	Organic and metal carbonyl derivatives of Ln(II)	1988	[13]
Shen Q et al.	π-Complexes, heterobimetallic systems involving Al	1988	[14]
Schumann H et al.	Bis(cyclopentadienyl) complexes - Se, P, As, Si, Ge	1988	[15]
Poli R	Monocyclopentadienyl halide complexes	1991	[16]
Evans WJ, Foster SE	Bis(pentamethylcyclopentadienyl) complexes	1992	[17]
Zhil'tsov SF et al.	Ethynyl complexes	1992	[18]
Zakharov LN	Complexes with non-transition elements Si, Ge, Sn	1992	[19]
Cloke FGN	Zero oxidation states	1993	[20]
Schaverien CJ	General developments from 1984–1994	1994	[21]
Gilje JW, Roesky HW	Organometallic hydroxy complexes	1994	[22]
Köhn R et al	Comprehensive general overview	1994	[23]
Evans WJ	Alternative ancillary ligand sets	1995	[24]
Soloveichik GL	Heterometallic complexes	1995	[25]
Schumann H	π-Complexes of Ln(III)	1995	[26]
Edelmann FT	Cyclooctatetraenyl complexes	1995	[27]
Edelmann FT	Cyclopentadienyl free organolanthanide chemistry	1995	[28]
Edelmann FT	Comprehensive general overview	1995	[29]

[a] Not included are the annual surveys in J Organomet Chem and Coord Chem Rev

Table 2. Review articles covering Ln–N and Ln–O based organolanthanide chemistry

Author(s)	Topic	Year	Ref.
L–N			
Eller PG et al.	Silylamides	1977	[30]
Birnbaum ER, Forsberg JH	Silylamides	1986	[31]
Edelmann FT	Complexes with heteroallylic ligands	1994	[32]
Santos I, Marques N	Poly(pyrazolyl) borate complexes	1995	[33]
Ln–O			
Birnbaum ER	General overview	1981	[34]
Mehrotra RC et al.	Coordination chemistry of complexes with Ln–O bonds	1980	[35]
Mehrotra RC	Alkoxide and aryloxide complexes	1991	[36]
Hubert–Pfalzgraf LG	Design of homo- and heterometallic complexes	1995	[37]

Table 3. Review articles covering applied organolanthanide chemistry

Author(s)	Topic	Year	Ref.
Organic synthesis/catalysis			
Kagan HB, Namy JL	Yb(II) and Sm(II) in organic synthesis	1984	[38]
Watson PL, Parshall GW	Organolanthanides in catalysis	1985	[39]
Kagan HB, Namy JL	Lanthanides in organic synthesis	1986	[40]
Long JR	β-Diketonates in organic synthesis	1986	[41]
Shen Z, Ouyang J	Coordination catalysis in stereospecific polymerization	1987	[42]
Kahn B, Rieke RD	Carbonyl coupling reactions	1988	[43]
Kagan HB et al.	Organic chemistry induced by Sm(II)	1988	[44]
Imamoto T	Organocerium reagents	1991	[45]
Molander GA	Samarium and ytterbium reagents	1991	[46]
Molander GA	Lanthanide reagents in organic synthesis	1992	[47]
Yasuda H, Tamai H	Polymerization initiators	1993	[48]
Material sciences[a]			
Hubert-Pfalzgraf LG	Alkoxide complexes as sol gel precursors	1987	[49]
Bradley DC	Alkoxide complexes as OMCVD precursors	1989	[50]
Deacon GB	CVD of β-diketonate and cyclopentadienyl complexes	1990	[51]
Sanchez C, Livage J	Alkoxide complexes as sol gel precursors	1990	[52]
Hubert-Pfalzgraf LG	Alkoxide and β-diketonate precursors for thin films	1992	[53]
Chandler CD et al	Precursor for perovskite-phase mixed-metal oxides	1993	[54]
Bazuev GV, Kurbatova LD	β-Diketonate precursors for superconducting ceramics	1993	[55]
Schulz DL, Marks TJ	MOCVD precursors for superconducting electronics	1994	[56]

[a] Only the article of Deacon et al. is entirely devoted to the lanthanide topic

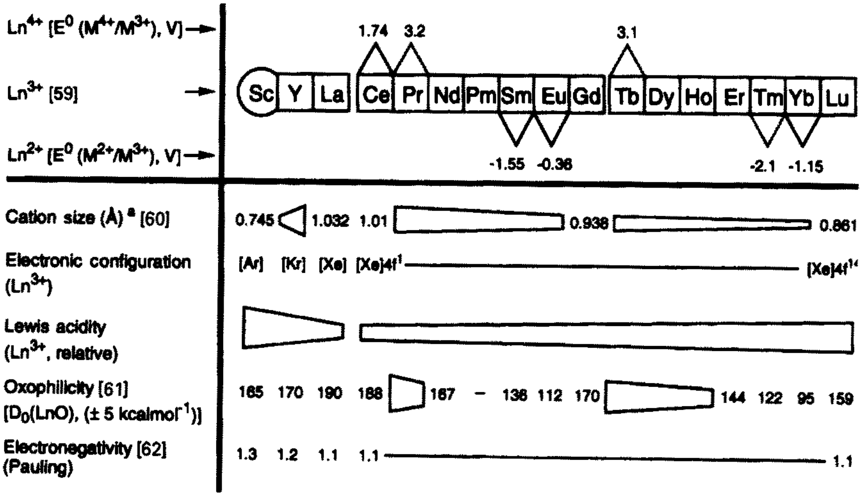
In this article, the authors want to work out the relationship between the intrinsic properties of a lanthanide element and an organic ligand, which frequently leads to an intriguing synergism in organolanthanide chemistry. The consideration of specific properties of the lanthanide cations as well as thermodynamic and kinetic factors is crucial for the design and the directed synthesis of molecular compounds.

2 Element(-Cation) Guidelines

The highly electropositive character of the lanthanide metals, which is comparable to that of the alkali and alkaline earth metals, leads as a rule to the formation of predominantly *ionic* compounds, Ln(III) being the most stable *oxidation state* [58]. Scheme I outlines this and other intrinsic properties of the lanthanide series and will serve as a point of reference in this section [59–62]. In the following, electronic and steric properties are treated separately.

2.1 Electronic Considerations

The Ln(III) cations of the series Ce-Lu possess the extended Xe-core electronic configuration [Xe] $4f^n$ (n = 1–14), a symbol which perfectly pictures the limited radial extension of the f-orbitals: The 4f shell is embedded in the interior of the ion, well shielded by the $5s^2$ and $5p^6$ orbitals [63]. A plot of the radial charge densities for the $4f$, $5s$, $5p$ and $6s$ electrons for Gd^+ visually explains why Ln(III) cations are commonly thought as a "*tripositively-charged closed shell inert-gas electron cloud*" (Fig. 1) [63].



Scheme I. Trends within intrinsic properties of Ln(III) cations and Ln elements. a Effective ionic radii for 6-coordination (see also Table 4)

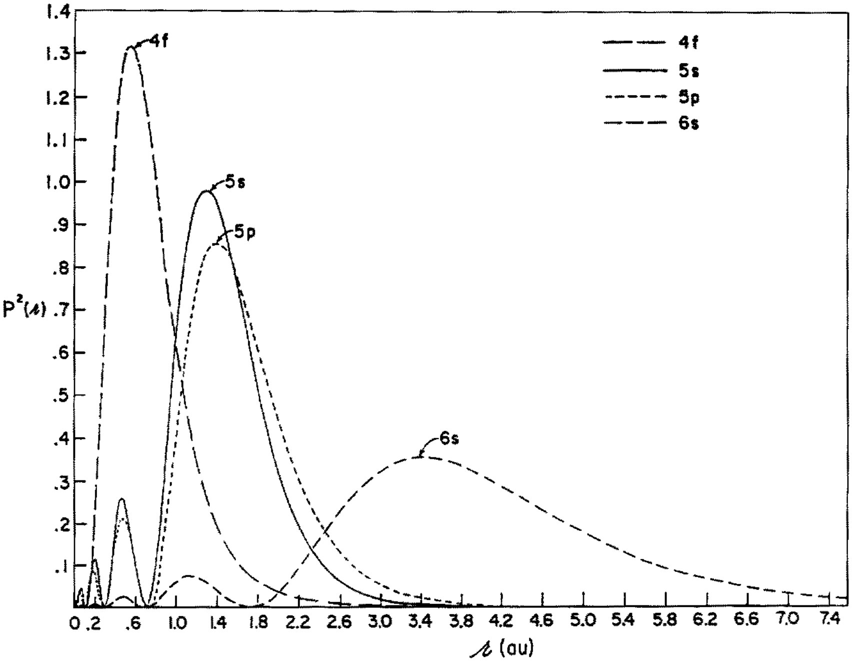


Fig. 1. Plot of the radial charge densities for the 4*f*, 5*s*, 5*p*, and 6*s* electrons of Gd$^+$, from [63]

Ionization energies of the elements [64], optical properties [65] and magnetic moments of numerous complexes [66] prove that the *f*-orbitals are perfectly shielded from the effects of the field of surrounding anions. Complexation of dipolar molecules results in minimal perturbation of the electronic transitions between the energy levels of the *f*-orbitals. In contrast to the broad $d \rightarrow d$ absorption bands of the transition elements, the $f \rightarrow f$ bands of the lanthanides in solid and in solution are almost as narrow as they are for gaseous ions. These "Laporte forbidden" transitions result in weak intensities which determine the pale colors of the complexes. Due to the "hidden orbitals", interaction with ligand orbitals is limited and consequently the colors of the trivalent species in general do not vary as the nature of ligation is changed. The σ-donor/ π-acceptor bonding mode is absent and lanthanides do not form classic carbene, carbine, or carbon monoxide complexes (no 18 electron rule!); neither Ln = O or Ln ≡ N bonds have been observed. On the other hand, the lack of orbital restrictions, e.g., the necessity to maximize orbital overlap as in *d*-transition metal chemistry, allows "symmetry forbidden" reactions. For the reasons of very small crystal-field splitting and very large spin-orbit coupling (high Z) the energy states of the $4f^n$ electronic configurations are usually approximated by the Russel-Saunders coupling scheme [67].

This orbital constellation also implies a *conform chemical behavior* of the Ln(III) derivatives. The importance of this electronic situation is evident and promising in numerous intriguing optical and magnetic applications ("probes in life") [64]. On the other hand, it seems at a first glance to be rather boring in view of any exciting reaction patterns that should be expected in passing through this 17-series.

The contracted nature of the 4*f*-orbitals and the concomitant poor overlap with the ligand orbitals contribute to the predominantly ionic character of organolanthanide complexes. Consequently, metal ligand interactions are determined by electrostatic factors. The attribute "ionic" is particularly evident in reactions where lanthanide cations preferentially interact with "hard" ligands to form often structures of irregular geometry that exhibit a variety of coordination numbers. According to the HSAB classification of Pearson [68], lanthanide cations are considered as ***hard acids***, being located between Sr(II) and Ti(IV). As a consequence, alkoxide, amide and cyclopentadienyl ligands show almost constant effective ligand anion radii (alkoxide, 2.21 ± 0.03 Å; silylamide, 1.46 ± 0.02 Å; cyclopentadienyl, 1.61 ± 0.03 Å) [69] and therefore fit into the evaluation criteria for ionic compounds according to Eigenbroth and Raymond [70]. The ionic-bonding contributions cause the strong *oxophilicity* of the lanthanide cations which can be expressed, for example, in terms of the dissoziation energy of LnO [61]. The interaction of the oxophilic metal center with oxygen-containing substrate molecules is often an important factor for governing chemo-, regio- and stereoselectivities in organolanthanide-catalyzed transformations [41]. Complexation of the "softer" phosphorus and sulfur counterions is applied for detecting extended covalency in these molecular systems [71, 72].

Scheme I further indicates the tendency of the Ln(III) cations to form the more unusual oxidation states in solution [73]. Hitherto, organometallic compounds of Ce(IV), Eu(II), Yb(II) and Sm(II) have been isolated. Charge-dependent properties, such as cation radii and Lewis acidity, significantly differ from those of the trivalent species (Table 4). Ln(II) and Ce(IV) ions show very intense and ligand-dependent colors which is attributed to Laporte-allowed 4*f*→ 5*d* transitions [65b]. Complexes of Ce(IV) and Sm(II) have acquired considerable importance in organic synthesis due to their strong oxidizing and reducing behavior, respectively; their reaction patterns have been reviewed in detail [40, 44–47, 74]. Catalytic amounts of compounds containing the "hot oxidation states" also initiate substrate transformations; as a rule this implies switch to the more stable, catalytically-acting Ln(III) species [75].

2.2 Steric Considerations

Of course, the fascinating steric features of lanthanide elements are most impressively expressed in the *lanthanide contraction* [76]. In textbooks, lanthanide contraction is often simply explained as being the phenomena responsible for similar chemical properties, in particular between the pairs of the *d*-transition metal homologues Zr/Hf, Nb/Ta and Mo/W. However, what does the contraction mean to the lanthanide elements (and compounds derived from them)

Table 4. Effective ionic radii for Ln(III), Ln(IV) and Ln(II) after Shannon [60][a]

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

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

themselves? The atomic (with exceptions) and the ionic radii decrease monotonically with increasing atomic number. It is only this feature of contraction that decisively favors the industrial separation of these elements. Of course, this unique behavior, which originates from the above-mentioned directional characteristics of the 4*f*-orbitals is enhanced by the electrons added along the series between La and Lu. The 4*f*-electrons do not shield each other efficiently from the growing nuclear charge and as a result contraction occurs.

Scheme I and, in more detail, Table 4 represent the trend of ionic radii of these "*large cations*" which prefer formal coordination numbers in the range of 8–12 [77]. For example, considering the effective Ln(III) radii for 9-coordination, a discrepancy of 0.164 Å allows the steric fine-tuning of the metal center [60]. The structural implications of the lanthanide contraction can be visually illustrated by the well-examined homoleptic cyclopentadienyl derivatives (Fig. 2) [78]. Three structure types are observed, depending on the size of the central metal atom: **A**, $[(\eta^5-Cp)_2Ln(\mu-\eta^5\colon \eta^x-Cp)]_\infty 1 \leq x \leq 2$; **B** $Ln(\eta^5-Cp)_3$; **C**, $[(\eta^5-Cp)_2Ln(\mu-\eta^1\colon \eta^1-Cp)]_\infty$; these exhibit coordination numbers of 11 (10), 9, and 8, respectively. Also a small change in ligand substitution leads to a change in coordination behavior and number (10), as

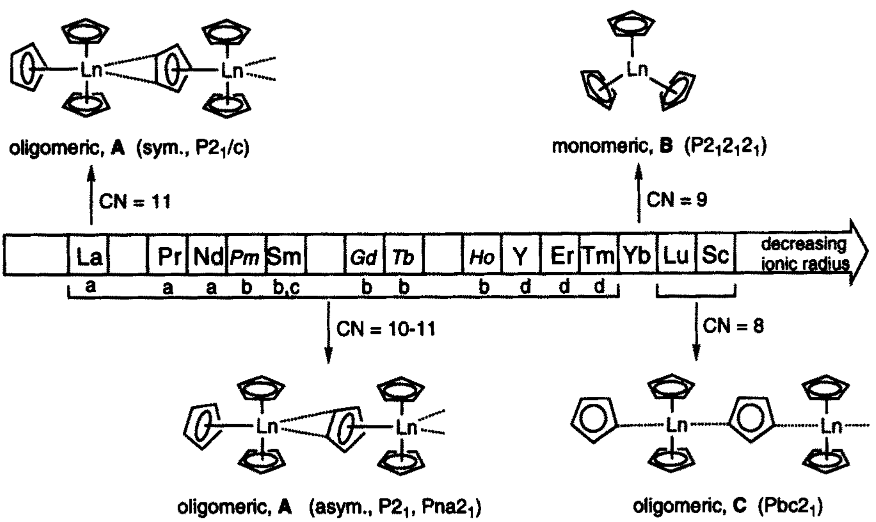


Fig. 2. Coordination modes in homoleptic, ionic $LnCp_3$ derivatives (*a*: belong to space group $P2_1$; *b*: indication from a powder diffraction pattern; *c*: show additional the modifications Pbcm and $P2_1/n$ (contact dimer-effect of crystallization conditions [78b]); *d*: belong to space group $Pna2_1$ and exhibit lengthened intermolecular Ln–C contacts)

found in the "MeCp" derivative. Monomeric type **B** is preferentially formed with ligands bearing bulky substituents.

High coordination numbers can usually be accomplished in oligomeric structures or highly solvated complexes. However, both forms are undesirable for synthesizing highly reactive compounds. The reactivity and stability, respectively, of lanthanide complexes is correlated with the steric situation at the metal center. Evaluation criteria as the principle of "steric saturation/unsaturation/oversaturation" have been developed to explain the differences in reactivity [12]. The synthetic chemist is challenged by the fine-tuning of the ligand sphere to obtain tractable (volatile, catalytically reactive, etc.) compounds. Because of the importance of steric factors, ligand environments have been numerically registered, e.g., by the "cone-packing model" [79], which represents a 3-D extension of Tolmans "cone-angle model" [80]. In this model, so-called solid angles are calculated from structural data employing van der Waals radii [81] and considering the effects of second-order packing. The introduction of steric coordination numbers, which are based on solid angle ratios, further emphasize the importance of steric considerations in organo-*f*-element chemistry [82].

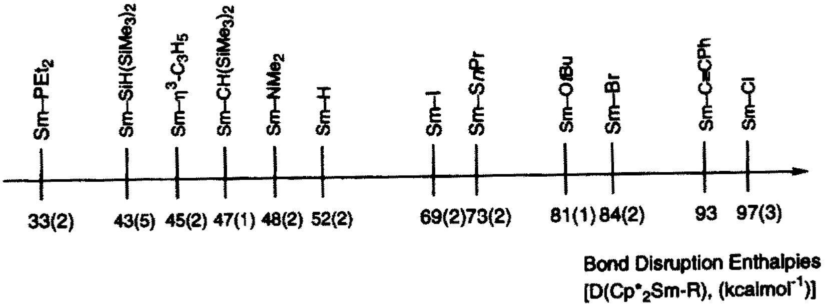
The *Lewis acidity* which is affected by the charge density (Z/r) is less distinct in complexes derived from the large Ln(III) cations. Hence these systems are often reported as mild Lewis acidic catalysts in organic synthesis [41]. However, Sc(III), as the smallest Ln(III) cation by far, is located in a "pull position", not only with respect to Lewis acidity, and its "aluminum/lanthanide/early transition metal hybrid character" [83] revealed its superiority in many catalytic applications [83, 84]. Because of their relative preferences for pyridine, Lappert suggested a relative Lewis acidity scale: $Cp_2ScMe > AlMe_3 > Cp_2YMe \approx Cp_2LnMe$ (here: Ln = large lanthanide elements) [85]. Maximum electrostatic metal/ligand interaction (enhanced *complex stability*) is also expected for scandium because increasing cation radii reduce both electrostatic interactions and ionic bond strength. The Ln(III) charge density and the concomitant complexation tendency prove to be favorable in the use of lanthanides as spectroscopic and magnetic probes to study the nature of Ca^{2+} binding in biological macromolecules [64].

3 Thermodynamic and Kinetic Considerations

Marks et al. provided a valuable examination of the absolute bond-disruption enthalpies of various important organometallic ligands R in $Cp^*_2Sm{-}R$ [86]. The data obtained by anionic iodinolytic and alcoholytic isoperibol titration calorimetry (performed in toluene) were calculated according to Scheme II. The knowledge of these absolute bond disruption enthalpies helps towards a better

$$\begin{array}{rcllr}
Cp^*_2Sm{-}R + X_2 & \longrightarrow & Cp^*_2Sm{-}X + RX & \Delta H_{rxn}(1) & (a)\\
Cp^*_2Sm{-}X & \longrightarrow & Cp^*_2Sm + 0.5\,X_2 & \Delta H_{rxn}(2) & (b)\\
X^{\bullet} & \longrightarrow & 0.5\,X_2 & -0.5\,D(X{-}X) & (c)\\
R{-}X & \longrightarrow & R^{\bullet} + X^{\bullet} & D(R{-}X) & (d)\\
\hline
Cp^*_2Sm{-}R & \longrightarrow & Cp^*_2Sm + R & & (e)
\end{array}$$

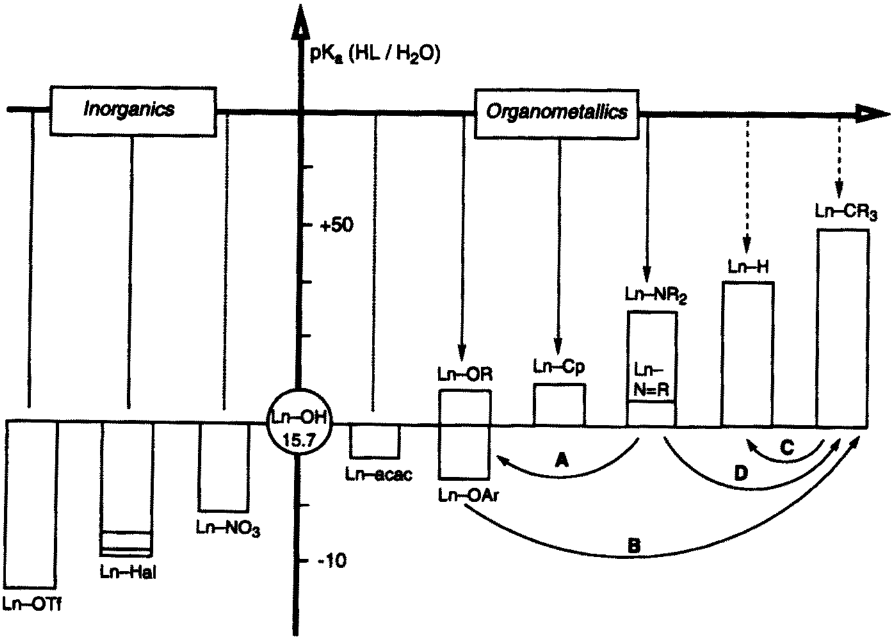
$$D(Cp^*_2Sm{-}R) = \Delta H_{rxn}(1) + \Delta H_{rxn}(2) - 0.5D(X{-}X) + D(R{-}X)$$



Scheme II. Bond-disruption enthalpies of organosamarium(III) complexes analysis of the thermodynamics of archetypal ligand-exchange reactions and judging the mechanistic scenarios of catalytic transformations [87]. The data are in agreement with the results obtained by an empirical "catimer/animer-model" [88].

Scheme III encompasses the different classes of compounds which are involved in organolanthanide chemistry by considering both the most important organic ligands and their inorganic precursors, as well as by indicating preferred synthetic strategies. Organic ligands usually possess a strongly basic character. As acid-base-type exchange reactions are fundamental to organolanthanide chemistry, the ligands are depicted according to their increasing pK_a values (in water) and this also correlates with the tendency to hydrolyze (organometallics) or with the competition between solvation and complexation (inorganics).

The central point in this consideration is the Ln-OH moiety, the preferred formation of which is considered to be a dilemma in organolanthanide chemistry. Organolanthanide compounds containing Ln-X σ-bonds such as alkyls, amides and alkoxides readily hydrolyze when exposed to moist air, with the formation of the hydroxides. Lanthanide complexes with Ln-C linkages are considered to be "oversensitive" compounds [89]. Even ligands with lower pK_a values than water, as exemplified by substituted phenol ligands, tend to hydrolyze in organic solvents because the insoluble hydroxides formed act as



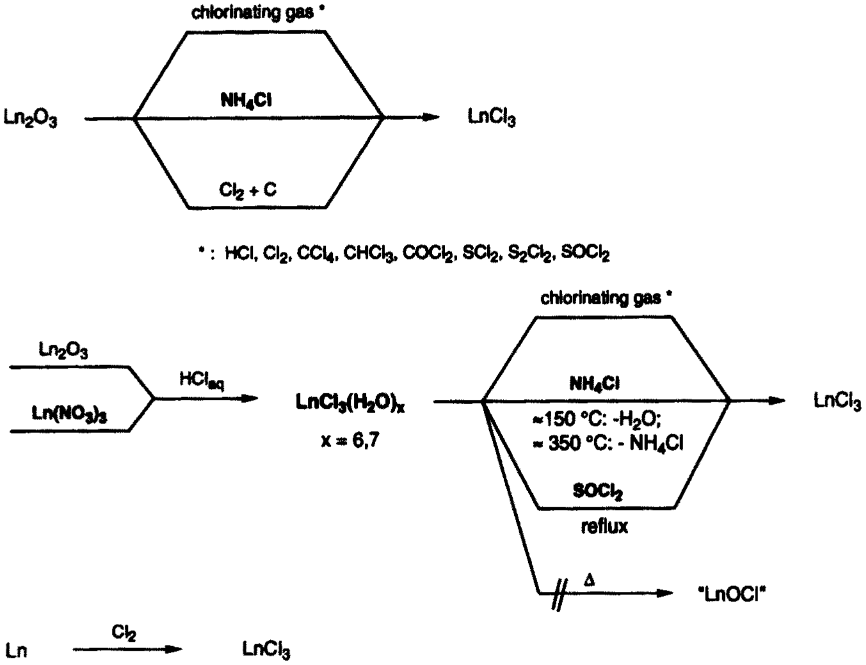
Scheme III. Synthetic strategies towards organolanthanide compounds a driving force. However, the presence of hard donorfunctionalities or multiply-charged anions, which are capable of chelatization, can afford moisture-stable alkoxide and amide complexes, as has been shown for binaphthol [90], polypyrazolylborate [91] and porphyrin-like complexes [92]. In addition, alkoxide complexes derived from small alcohol ligands tend to form mixed oxy-/hydroxy-complexes in the presence of traces of water [93]. In these systems the oxy- and hydroxy-moieties occupy central cluster positions where they can accomplish high metal coordination ($\leqslant 6$) . Partially hydrolyzed compounds, particularly derivatives containing bridging hydroxy-groups can be synthesized by specific hydrolysis in very dilute solutions [94].

3.1 Inorganic Reagents

Of course, thermodynamic and kinetic considerations for the synthesis of intrinsic organometallics have to deal with appropriate starting materials. The availability of both pure and dehydrated starting compounds and dry organic solvents [95] is crucial for the synthesis. Anhydrous lanthanide halides are the most important reagents in this regard and are therefore treated in detail [96–106]. As a rule, in complexes with strong monobasic acids or even superacids, cation solvation competes with anion complexation and the solid state structures reveal fully or partly separated anions and solvated cations. The extent of solvation contributes to the reactivity of the inorganic material. This tendency to form outer-sphere complexation in coordinating solvents [107] is one criteria for evaluating the suitability of inorganic salt precursors in organometallic transformations.

Ln-Halides. The complexation/solvation criteria is just one reason why lanthanide halides are the most common precursors in organolanthanide chemistry. In this evaluation, lanthanide iodides are often preferred to bromides and chlorides, however the former are more difficult to synthesize and are much more expensive [96f]. Waterfree, solid Ln-halides are ionic substances with high melting points which immediately absorb water when exposed to air, forming hydrates ($I^- > Br^- > Cl^-$). Therefore, they have to be handled under an inert gas atmosphere. The main use of the halides is for the production of pure metals [96]. Some methods of preparing Ln(III)-chlorides are summarized in Scheme IV [96].

For laboratory use, the dehydration of $LnCl_3 \cdot (H_2O)_x$ ($x = 6, 7$) using NH_4Cl is the favorite method of preparing anhydrous lanthanide chlorides [96b]. However, simple thermal dehydration, as accessible to lanthanide triflates, leads to the formation of undesirable lanthanide oxychlorides. Because the Ln-halide precursor is insoluble in aliphatic and aromatic hydrocarbons, the preparation of organolanthanides via salt metathesis is performed in coordinating solvents such as THF.



Scheme IV. Methods of preparing $LnCl_3$

These reactions proceed via the initial formation of the solvated "Ln(halide)$_3$(THF)$_x$" compounds, which are assumed to be the reactive Ln-components [97]. The THF adducts display a rich coordination chemistry, as indicated by the various solid state structures that are obtained by varying the crystallization conditions (Fig. 3) [98–102]. The specific formation of the more reactive monomeric species and the stepwise/complete replacement of the THF ligands by other coordinating moieties to yield more or less solvated cation–anion pairs might have significant implications in reaction chemistry. Donor moieties such as ε-caprolactone [102], 2,6-dimethyl-4-pyrone [103] or chelating ligands such as DME [104] and crown ethers [105, 106] reveal unforseen and intriguing coordination chemistry.

Therefore, for small-scale laboratory synthesis it seemed promising to develop alternative methods which avoid the "inconvenient" high temperature and yield the reactive, solvated form. For example, the THF adducts can readily be synthesized by treating lanthanide powders with $CHCl_3$ under ultrasonic conditions, as described by Eq. (1) [100]. Redox transmetallation between lanthanide metals and mercury(II) halides are carried out in refluxing THF (Eq. 2) [108]. Recently ammonia was employed as an alternative solvent, e.g. in the synthesis

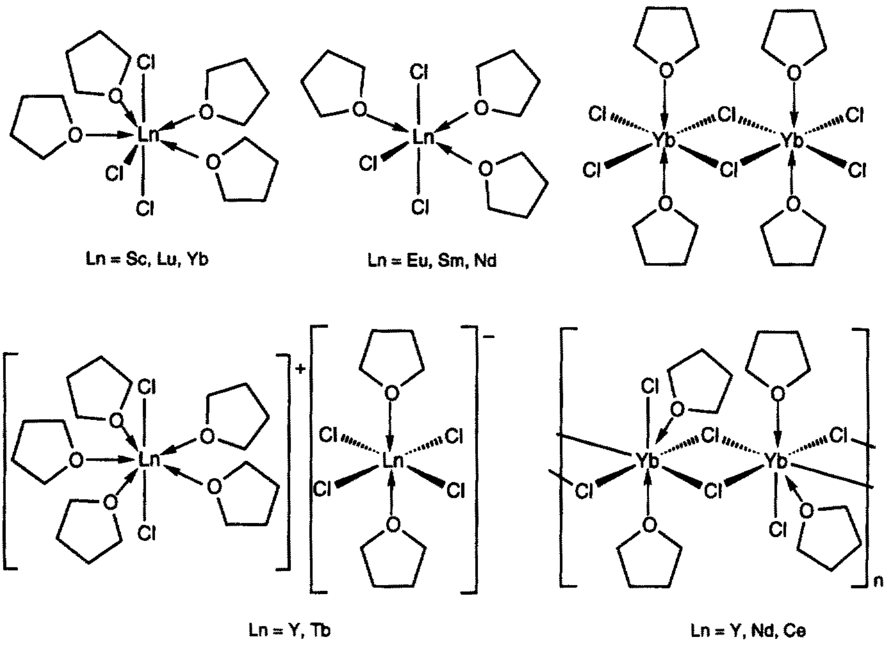


Fig. 3. Solid state structures of THF-solvated Ln(III) chlorides

of lanthanide alkoxides starting from lanthanides chlorides [109].

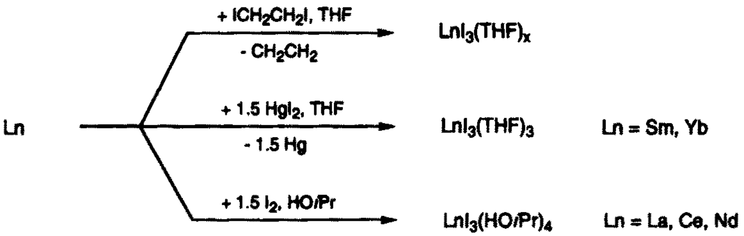
$$2\,\mathrm{Ln} + 3\mathrm{C_2Cl_6} \xrightarrow[))]{\mathrm{THF}} 2\,\mathrm{LnCl_3(THF)}_x + 3\mathrm{C_2Cl_4} \tag{1}$$

$$2\,\mathrm{Ln} + 3\,\mathrm{HgCl_2} \xrightarrow[\Delta]{\mathrm{THF}} 2\,\mathrm{LnCl_3(THF)}_x + 3\,\mathrm{Hg} \tag{2}$$

$$\mathrm{Ln} = \mathrm{Yb}(x = 3);\ \mathrm{Er}(x = 3.5);\ \mathrm{Sm}(x = 2);\ \mathrm{Nd}(x = 1.5)$$

Preparation of lanthanide bromides and iodides is performed under similar but aggravating conditions, according to Scheme IV [96f]. Small-scale syntheses of solvated iodides are given in Scheme V [110–112]. Strongly donating solvents such as *N*-methylimidazole (*N*-MeIm) can accomplish complete anion–cation separation, as has been shown for $[\mathrm{Sm}(N\text{-MeIm})_8]\mathrm{I}_3$ under anaerobic conditions [113].

As a rule, lanthanide bromides, and more especially the iodides, are more reactive because of their often higher solubility (Table 5), and also show enhanced thermodynamic lability (Scheme III). Moreover, reactivities different from those of the chloride analogues should be expected because of, for example, the softer Lewis basicity of the iodide anion and different solubility properties of the eliminated alkali salts. Table 5 gives an arbitrary sample of solubilities for lanthanide halides in various standard-laboratory donating solvents [97f].



Scheme V. Small-scale syntheses of solvated Ln(III) iodides

Table 5. Solubility of lanthanide halides in nonaqueous coordination solvents (g/100 g solvent) [96f]

LnX_3/solvent	Ether	THF	Diglyme	Py	DMF	TBP	Structural type (CN)
$NdCl_3$	0.006	1.16	0.04	1.8	0.2	31.8	UCl_3 (9)
$YbCl_3$	0.085	1.98	1.4				$AlCl_3$ (6)
$NdBr_3$		0.71		109.2			$PuBr_3$ (8)
$YbBr_3$		0.25					$FeCl_3$ (6)
NdI_3					657.1		$PuBr_3$ (8)
TbI_3		8.63					BiI_3 (6)

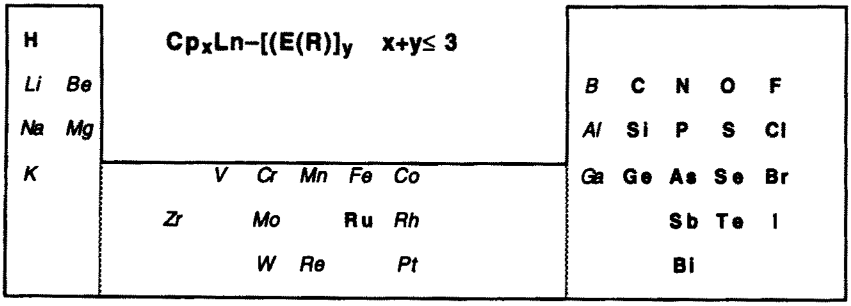


Fig. 4. Organometallic lanthanide/heteroelement systems (**bold**: complex with direct Ln-E bond; *italic*: Ln and E in the same molecule)

As can be seen from Scheme III, lanthanide halides are suitable precursors for the synthesis of homoleptic derivatives such as silylamides [114], cyclopentadienyls [115] and aryloxides [116]. Such organometallics can be readily obtained in a pure form by sublimating them from the reaction mixture. They themselves are important precursors in organometallic transformations (vide infra). Heteroleptic complexes of the type $Cp_xLn(halide)_y$ $(x + y = 2, 3)$ are important synthetic precursors with respect to formation of various Ln-X bonds via simple metathesis reactions [2–29]. Fig. 4 indicates the lanthanide element bonds which are involved in these ubiquitous heteroleptic cyclopentadienyl systems.

Lanthanide(II) halides, in particular the iodides, are the only precursors to corresponding Ln(II) organometallics that have been examined (Eq. 3–5) [12, 117, 118]. SmI_2 is usually applied (in form of a THF solution) in organic synthesis [74]. Very recently, the determination of the molecular structure of a 7-coordinate $SmI_2(THF)_5$ compound was achieved [119]. The large-scale synthesis of $SmBr_2$, avoiding the expensive metal precursor, could be accomplished according to the reaction sequence shown in Eq. (4) [117]. $(pyH)_2(CeCl_6)$ has been discussed as an alternative Ce(IV) precursor [120].

$$Sm + ICH_2CH_2I \xrightarrow{THF} SmI_2(THF)_x + CH_2{=}CH_2 \tag{3}$$

$$Sm_2O_3 \xrightarrow{HBr_{aq.}} SmBr_3 \cdot 6H_2O \xrightarrow{\text{methyl orthoformate}}$$

$$SmBr_3 \xrightarrow{Li,\ THF} SmBr_2(THF)_x \tag{4}$$

$$Yb + 2NH_4I \xrightarrow{NH_3(liq)} YbI_2(NH_3)_x + H_2 \tag{5}$$

Pseudohalides, such as thiocyanates, should also receive some attention in the future. Because of their dual ligation mode, they might be used as specific synthetic precursors [121]. Like Ln-halides [122], they have been successfully employed as catalysts in organic transformations [123].

Others. Other inorganic precursors which are referred to in Scheme III are available by treatment of lanthanide oxides Ln_2O_3 with the corresponding acid [124, 125]. Nitrates form complexes slightly more easily than do the halides, but are reported to yield coarse precipitates of alkali nitrates in metathesis reactions [126]. Nitrates are also the preferred precursors in macrocyclic chemistry where they preferentially occupy the outer ligation sphere [57]. Strong complexation of doubly-charged anions ($CO_3^{2-} > SO_4^{2-}$) causes a considerable decrease in solubility of the corresponding Ln_2X_3 and hence precludes their broad use as synthetic precursors [125]. Ln-fluorides [127] and phosphates are totally insoluble in solvents suitable for organometallics [64]. However, the superacidic derivatives $Ln(OTf)_3$ [128] which are readily thermally dehydrated have attracted considerable attention as valuable anhydrous synthetic precursors [129] (Eq. 6).

$$Ln_2O_3 \xrightarrow[100\,^\circ C,\ 1\ h]{CF_3SO_3H,\ H_2O} [Ln(H_2O)_9][CF_3SO_3]_3 \xrightarrow[48\ h]{180-200\,^\circ C} Ln(CF_3SO_3)_3 \tag{6}$$

Cerium ammonium nitrate $(NH_4)_2Ce(NO_3)_6$ (CAN) is the most common precursor for Ce(IV) organometallics [130]. The use of acetylacetonates of cerium(IV) is discussed [131] and $Ce(OTf)_4$ might also prove to be a valuable precursor [132].

Metals. Lanthanide metals are also considered as valuable precursors. For example, alkoxides derived from cheap and low-boiling-point alcohols have been alternatively synthesized from metals in the presence of $HgCl_2$ as catalyst [133]. Representative and specific methods of preparation include transmetallation reactions (Eq. 7–9) [134], using ammonia solutions of ytterbium and europium as synthetic reagents (Eq. 10) [135] and the generation of thiolate complexes from disulfides (Eq. 11) [136].

$$\mathrm{Ln + 3\,TlCp \xrightarrow[80°\,C,\,20\,h]{THF} LnCp_3(THF) + 3Tl} \tag{7}$$

$$\mathrm{Sm + Hg(C_6F_5)_2 + 2\,HNR_2 \xrightarrow[12\,h]{THF} Sm(NR_2)_2(THF)_4 + Hg + 2\,HC_6F_5} \tag{8}$$

$$\mathrm{Yb + Sn[N(SiMe_3)_2]_2 \xrightarrow[80°\,C,\,8\,h]{THF} Yb[N(SiMe_3)_2]_2(THF)_2 + Sn} \tag{9}$$

$$\mathrm{Eu \xrightarrow{NH_3(liq)} Eu^{2+}(NH_3)_6 \cdot 2e^-(NH_3)_n \xrightarrow[-H_2,\,-NH_3]{HR} EuR_2(NH_3)_m} \tag{10}$$

$$\mathrm{Ln + 1.5\ ArSSAr \xrightarrow[50°C,\ Py]{I_2(!),\ THF} Ln(SAr)_3(Py)_3} \tag{11}$$

3.2 Organometallic Reagents

The incorporation of "inorganic anions" (halide contamination, formation of *ate* complexes), particularly as observed in alkyl [137] and alkoxide chemistry [138], by following the common salt metathesis route has produced new routes involving organic ligands only.

Considering the organometallic side of Scheme III (right), usually all the compounds located on this side are able to produce the neighboring systems on the left by Broensted acid-base-type reactions, e.g., alkyls might readily react with amines, cyclopentadienes and alcohols to yield amide, alkoxide and cyclopentadienyl complexes, respectively. The silylamide route has attracted enormous attention for the synthesis of pure alkoxides (**A** in Scheme III, Eq. 12) [139].

$$\mathrm{Ln[N(SiMe_3)_2]_3 + 3\,HOR \xrightarrow{hexane} Ln(OR)_3 + 3\,HN(SiMe_3)_2} \tag{12}$$

Lanthanide aryloxides have proved to be excellent precursors to homoleptic lanthanide alkyls (**B**, Eq. 13) [140]. The reaction can be conducted in non-polar solvents because of the good solubility of the starting compounds. The formation of insoluble alkali metal aryloxides is the driving force (kinetic control). Complexes derived from aliphatic alcohols [141] and acetylacetonates [131] are discussed as alternative alkyl precursors.

$$\mathrm{Ln(OAr)_3 + 3\,LiR \xrightarrow{hexane} LnR_3 + 3\,LiOAr} \downarrow \qquad (13)$$

A different synthetic procedure involves lanthanide amides as precursors to mixed metallic alkyls (**D**, Eq. 14) [142].

$$\mathrm{Ln(NMe_2)_3(LiCl)_3 \xrightarrow[-3\ LiCl]{exc.\ AlMe_3} Ln[(\mu - Me)_2AlMe_2]_3 +}$$

$$\mathrm{1.5\,[Me_2NAlMe_2]_2} \qquad (14)$$

Labile Ln-C(alkyl) bonds are disrupted by most protic reagents. The transformation Ln-C(alkyl)/Ln-H is of considerable interest for the synthesis of homogeneous lanthanide precatalysts (**C**, Eq. 15) [143].

$$\mathrm{Cp_2LnCH(SiMe_3)_2 + H_2\,(1\ atm) \xrightarrow[0^\circ C,\ 3\,h]{hexane}}$$

$$\mathrm{[Cp_2Ln(\mu-H)]_2 + H_2C(SiMe_3)_2} \qquad (15)$$

3.3 Thermal Stability

Despite the kinetic lability of the Ln-X-σ-bonds (even the thermodynamically very stable Ln-OR bond is subject to rapid ligand exchange reactions [49]) organolanthanide compounds are thermally very robust over a wide range of temperature (Fig. 5) [114, 116, 139, 144–151]. Thermal stability is not only favorable in catalytic transformations at elevated temperatures [47], for the support of volatile molecular precursors is of fundamental importance in chemical vapor deposition techniques; the sublimation behavior is a criterion of thermal stability and suitability for these processes (Fig. 5).

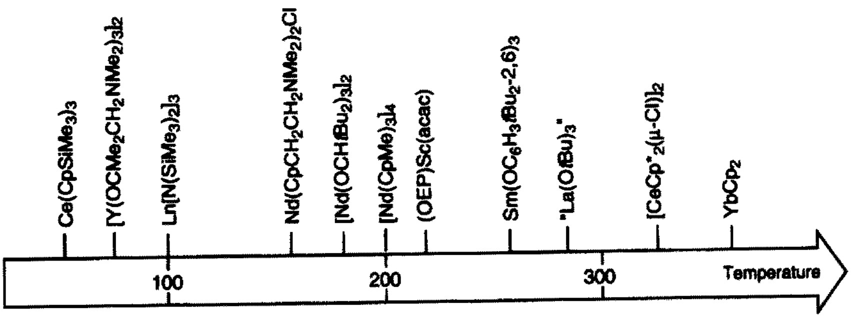
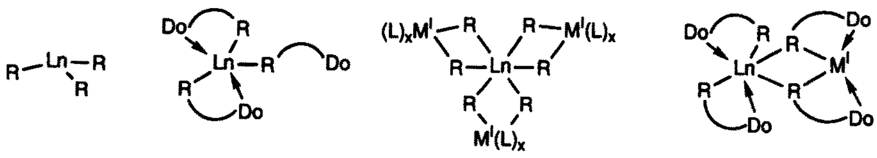


Fig. 5. Sublimation behavior of various lanthanide complexes at 10^{-3} mbar (OEP = 2, 3, 7, 8, 12, 13, 17, 18-octa(ethyl) porphyrin; acac = acetylacetonate)

Bulky ligands affect the ionic nature of the polarized Ln-X bond by minimizing the polar interactions (intra- and intermolecular) and optimizing volatility by the concept of steric shielding. The detection of isolated molecules instead of salt-like arrangements in the solid state confirms this trend. The polarizing effect can also be reduced by introducing donor-functionalized ligands which can bring about a transfer of charge to the metal cation. Decomposition pathways can be sterically blocked by filling the coordination sphere of the metal with large ligands. However, sterically overcrowded ligands may degrade at elevated temperatures, as illustrated in the Ln-tritox system [152].

4 Ligand Guidelines

Selection or design of an appropriate ligand sphere is of the utmost importance in organolanthanide chemistry. The nature of the ligand (type, size, basicity, capability of hard/soft ligand functionalities) promptly affects mononuclearity, cation size, Lewis acidity, etc., all of which co-determine the reactivity of the complex. Assuming the ligand interaction to be of electrostatic origin, optimal charge balance of the lanthanide(III) cations should be achieved by three stable anionic ligands. Identical anions will accomplish homoleptic systems of neutral type $(MR_n)_x$ or *ate* type $[MR_n]^{z-}$ $[X_m]^{z+}$ [153]. Bulky ligands should favor monomeric and volatile complexes, which are particularly required in the precursor chemistry of processes such as MOCVD. Homoleptic complexes are readily synthesized and guarantee pure deposition products. Homoleptic compounds can be further classified according to whether the ligands are coordinatively equally (*e-homoleptic*) or differently (*d-homoleptic*) attached to the metal center (Fig. 6). The *d-homoleptic* mode is found not only in oligomeric systems where both terminal and bridging ligands are present, but also in monomeric complexes which contain functionalized ligands. Here, steric oversaturation can prevent the formation of *e-homoleptic* coordination. As a result, dangling functionalities exist which are a nuisance with regard to volatility because they disturb the desired spherical shape [78]. On the other hand, such dangling groups can be valuable for synthesizing heterometallic complexes [154].



e-homoleptic *d-homoleptic* *ate-e-homoleptic* *ate-d-homoleptic*

Fig. 6. Modes of homoleptic Ln(III) coordination (Do = donor-functionality)

Considering homoleptic organolanthanide species the reader will get a rough overview of the ligands commonly examined. Figs. 7–10 classify structurally characterized complexes according to their shortest intramolecular Ln-X contact [155]. Figs. 7–9 show derivatives of Ln(III) in the upper half and

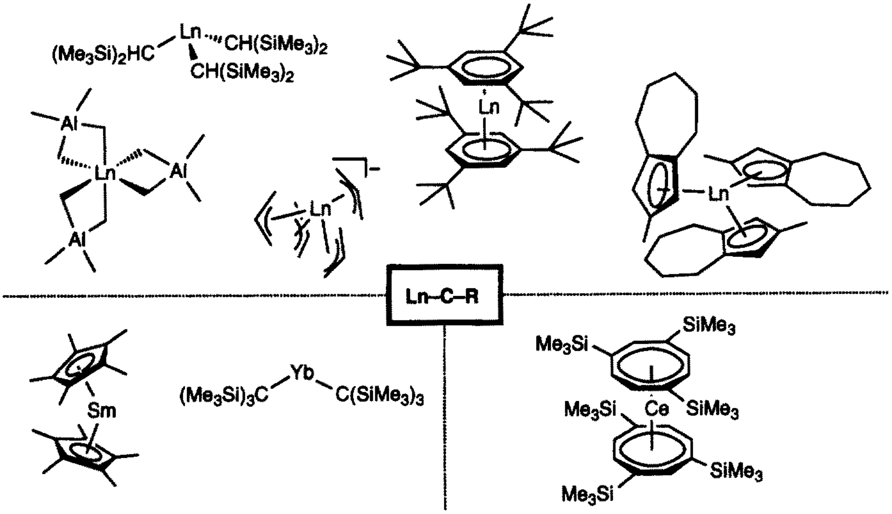


Fig. 7. Homoleptic complexes based on the Ln-C bond

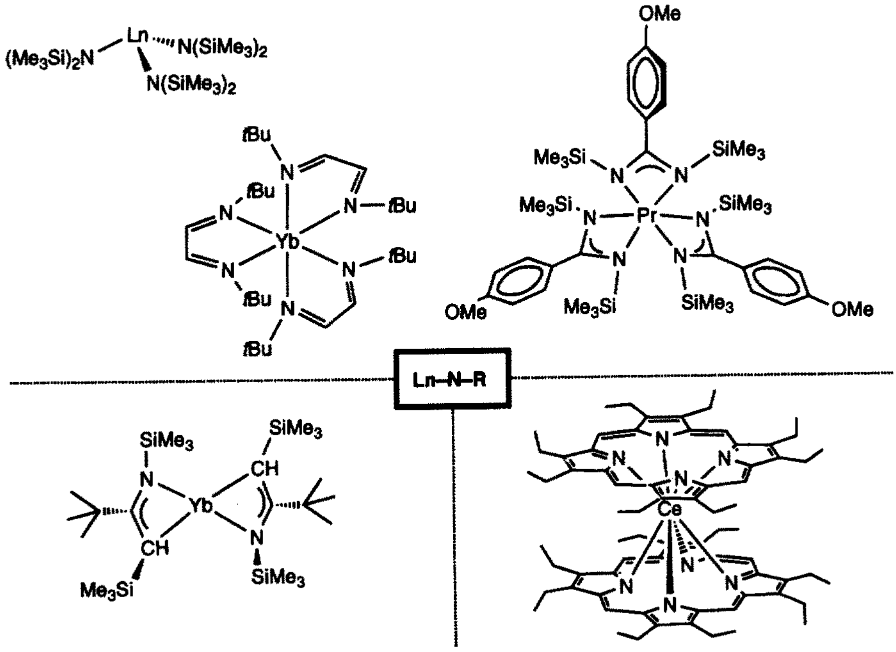


Fig. 8. Homoleptic complexes based on the Ln-N bond

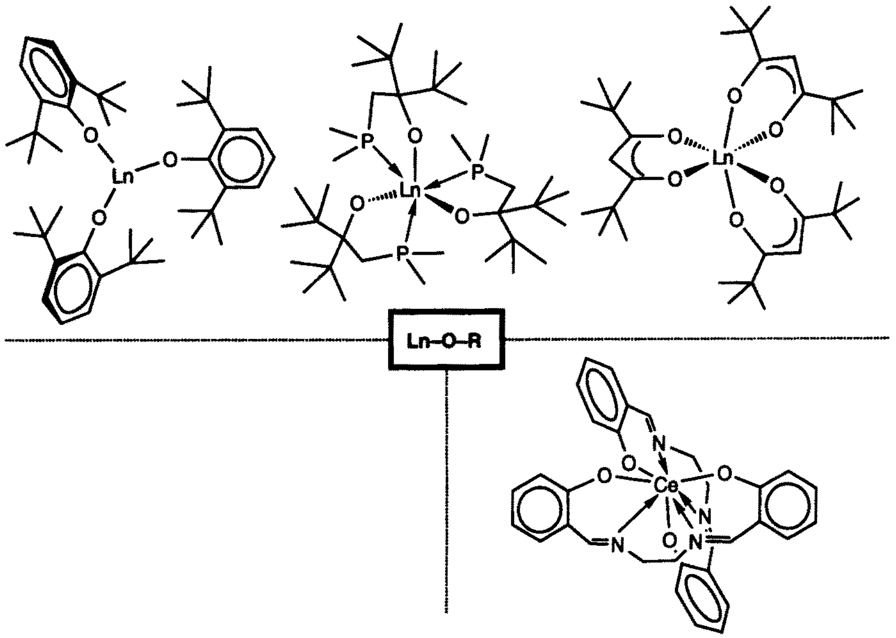


Fig. 9. Homoleptic complexes based on the Ln-O bond

derivatives of Ln(II) and Ln(IV), respectively, in the lower half. Ln-C bonded systems include alkyl [140, 142, 156], cyclopentadienyl [78, 115], pentadienyl [157], pentamethylcyclopentadienyl [158], indenyl [159], cyclooctatetraenyl [160], (aza) allyl [161] and arene derivatives [20] (Fig. 7). Representative examples of complexes based on Ln-N [20, 162–165] and Ln-O [166–169] are shown in Figs. 8 and 9 and treated in detail in the following articles. Homoleptic complexes derived from ligands containing higher homologous elements such as phosphorus and sulfur are summarized in Fig. 10 [134, 170, 171].

4.1 So-called "Spectator" Ligands

The term "spectator area" occupies a decisive part especially in the area of organolanthanide-catalyzed transformations. Spectator ligands might behave both passively (remain unchanged) and actively in the "game" catalysis. Properties such as mononuclearity, chemical resistance and rigidity which might be classified as typical attributes of a "passive backbone" of well-defined monolanthanide precatalysts behave ambivalently at second glance. For example, these spectator ligands are active if they cause metal shielding, if their bulkiness imposes steric restrictions, if differently polarized Ln-X bonds affect the Lewis acidity of the metal center, or if they offer a reservoir for chirality and additional flexible coordination sites.

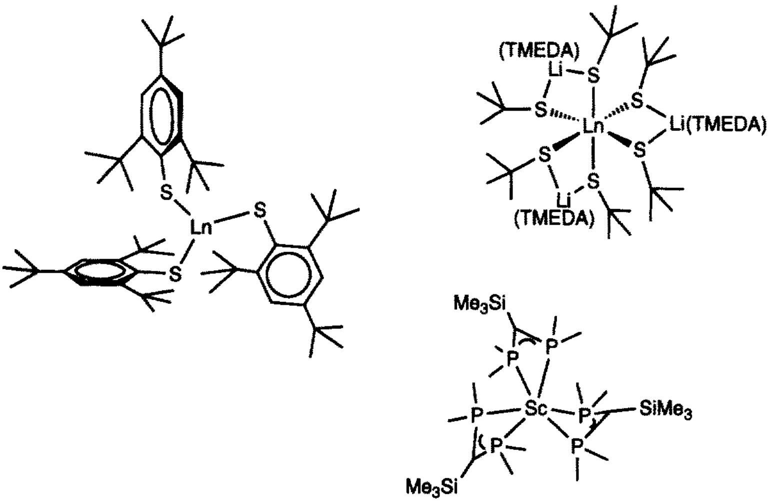
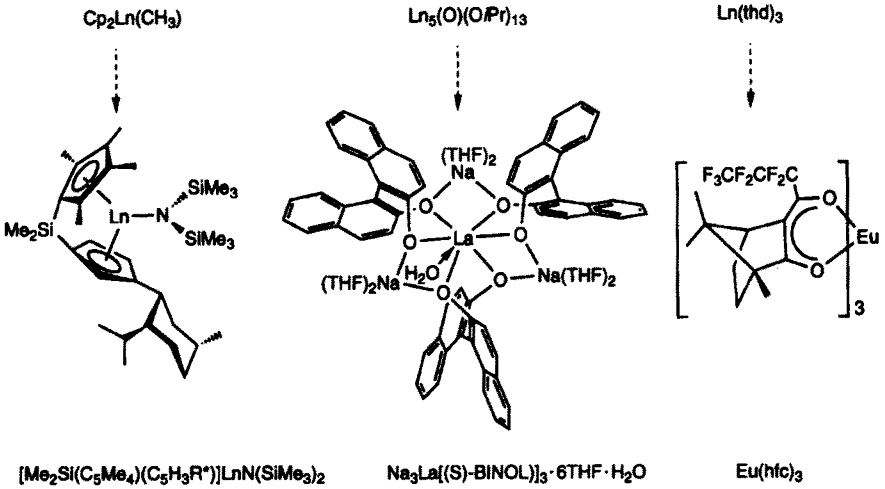


Fig. 10. Homoleptic complexes based on the Ln-S and Ln-P bonds

The efficiency of *f*-elements in catalysis originates from unconventional electrophilic pathways. In contrast to *d*-elements oxidative addition/reductive elimination sequences are not accessible. Instead, substrate adduct formation, ligand exchange and insertion reactions rule the mechanistic scenarios. Therefore, the main emphasis is put on the fine-tuning of the spectator ligand of the precatalyst.

Steric extension, substitution pattern and type of counterion (group organizing) directly affects the reactivity of the complex, as is impressively demonstrated by tied-back cyclopentadienyl complexes [83] and even water-stable binaphthol systems [90]. The required thermodynamic and kinetic stabilities are achieved by employing strongly-chelating or multiply-charged ligands and by making use of the entropy effect. Ligand design for lanthanide precatalysts has become indispensable because simple spectator areas usually lack suitable properties such as, for example, solubility, rigidity or asymmetric centers. Adaption of the prevailing precatalyst-types (cyclopentadienyl- [172], alkoxide- [90], β-diketonate-based [173]) to the requirements of highly enantioselective catalysis has gradually reached the high level of variety and sophistication, as is evidenced by the *d*-transition metals (Scheme VI) [174].

Scheme VII classifies potential spectator ligands according to their ligation mode. Ansa, doubly charged A-type ligands, have been prominent in catalytic investigations up to now and are usually employed in a neutral, heteroleptic form. The additional Ln-R moiety directs the catalytic reactivity in a non-spectator manner: Due to its kinetic lability, the Ln-R bond is accessible to ligand exchange reactions, as shown in *ansa*-cyclopentadienyl-supported catalysts for hydrogenation and polymerization reactions [83]. Biphenol or binaphthol ligands [175], the latter of which was recently successfully applied (e.g. in



Scheme VI. Development of sophisticated ligand environments for selective catalysis

Michael reactions) [176], have been considered as alternative A-type spectator environments. The transfer of the "catalytic substance" of Schiff-base ligands, established in the work of Jacobsen [177], should further stimulate research in this area since organolanthanide complexes, as depicted in Scheme VII, are now available [178].

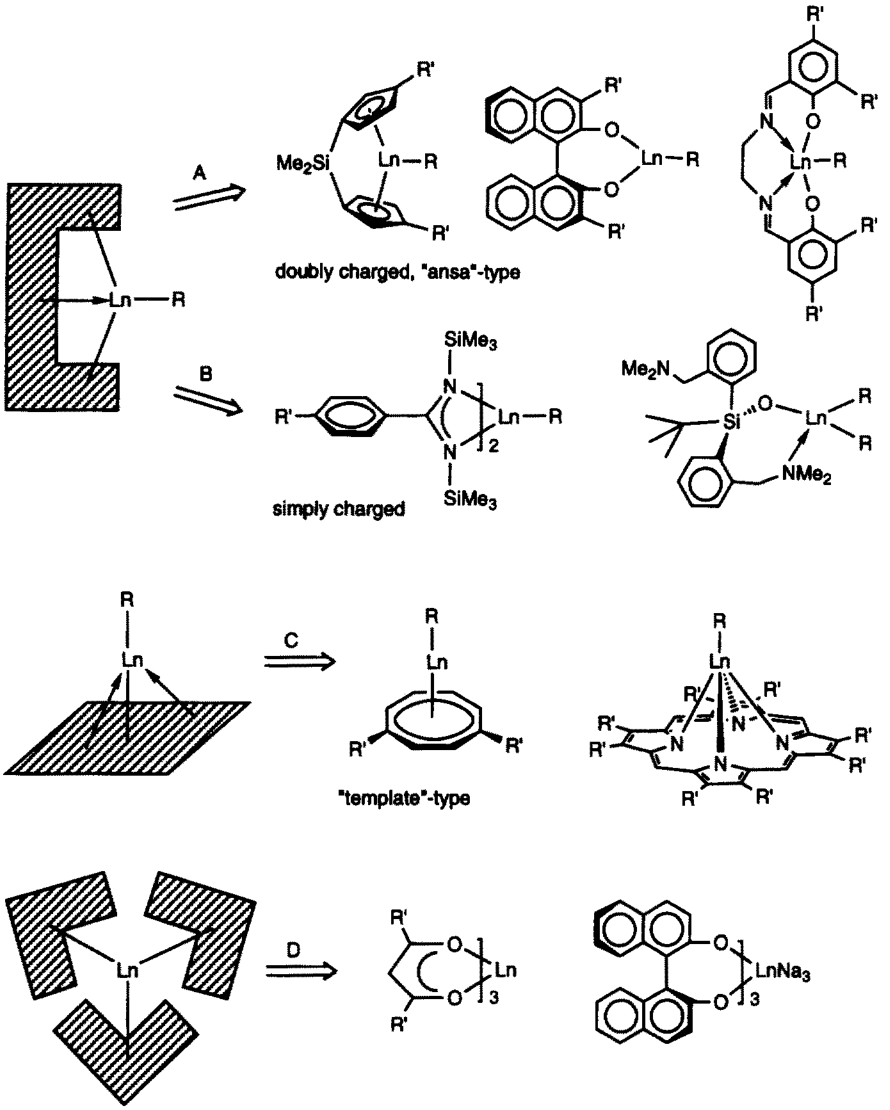
The heteroleptic B-type ligand sphere offers more steric flexibility. However, chelation by simple donor-functionalities can yield strongly-bonded ligand-metal moieties which are kinetically rather stable, as is shown, for example, in benzamidinate [179] or siloxide complexes [180].

C-type template ligands such as cyclooctatetraenyl [27] and porphyrin [181] have been shown to be very effective for stabilizing mononuclear complexes. In particular, porphyrin-type moieties are rather robust and less moisture-sensitive.

In homoleptic D-type systems such as Ln(β-diketonate)$_3$, catalytic activity is directed by the formation of Lewis acid (catalyst) /base (substrate) pairs [182]. Hence metal-ligand bond disruption and formation processes are pushed into the background.

4.2 Concept of Donor-Functionalization

No doubt, donor-functionalized ligands are becoming more and more popular in organolanthanide chemistry. The availability of donor-functionalities may be helpful not only in the fine-tuning of the above-mentioned spectator ligand environment. Intramolecular ring formation via "dative bonds" [183] can produce monomeric, homoleptic systems which show remarkable properties



Scheme VII. Classification of so-called spectator ligands (hatching indicates the spectator area)

such as enhanced volatility and moisture stability, properties required in the precursor chemistry of material-science technology. In the absence of ring strain, the bond strength of such an intramolecular coordination resembles that of the corresponding intermolecular one [184]. In numbers: the bond strength of an intramolecular hard "$\leftarrow OR_2$" coordination will be in the order of 7 kcal mol^{-1}, the same as that determined for intermolecular THF-coordination [86]. The following points emphasize the advantages gained by the presence of intramolecularly-active donor-functionalities:

(i) They increase the stability of the complex (effect of chelation and entropy).

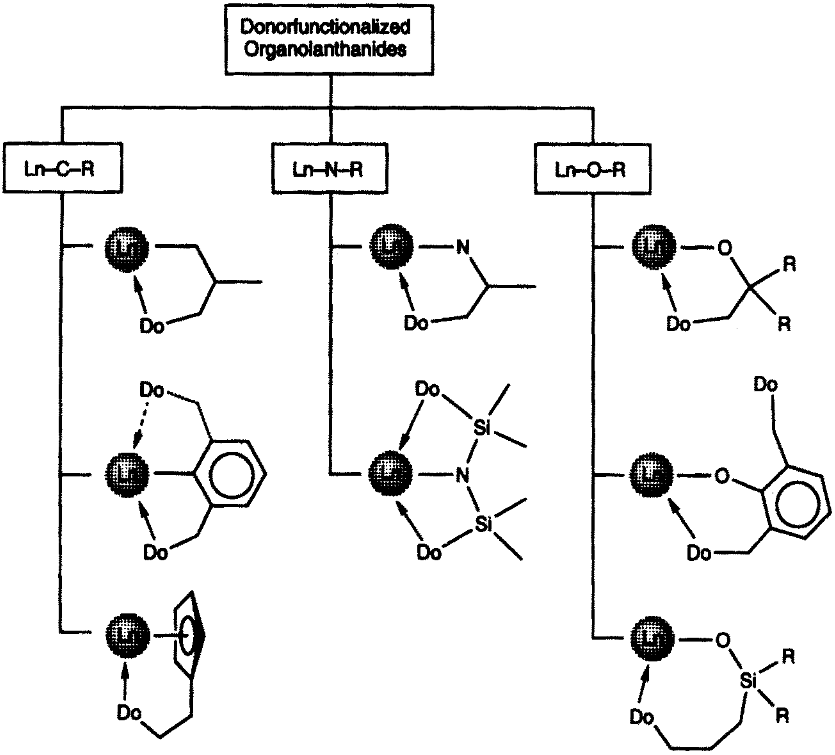
(ii) They will replace coordinating solvents, which usually separate off upon heating (thermally labile species), and hence they can prevent oligomerization during the heating period.

(iii) They affect the polarity of the lanthanide counterion bond by transferring more or less electron density into the metal, thus directing the reactivity of the complex (e.g., enhanced stability against hydrolysis).

(iv) They impose a flexible coordination mode at the metal center (hard-soft donor atoms; "arm on–arm off" process) which, for example, might influence the approach of organic substrates in catalytic transformations.

(v) They counteract salt and solvent inclusion.

Scheme VIII gives a representative selection of donor-functionalized ligands employed in the main classes of organolanthanide chemistry. Ln-O- and Ln-N-based systems are exhaustively treated in the following articles of this book [185–188]. Donor-functionalization is also applied as a route to thermally stable



Scheme VIII. Donor-functionalized ligands applied in organolanthanide chemistry

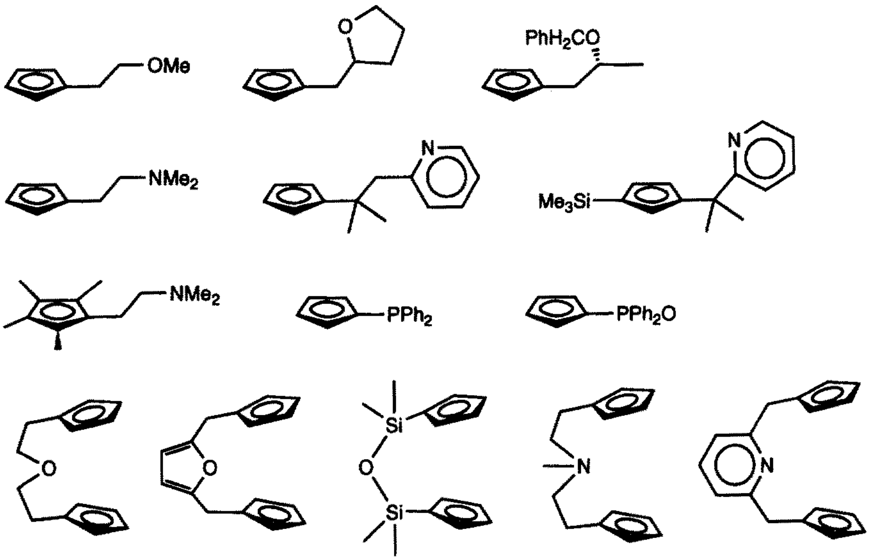


Fig. 11. Functionalized cyclopentadienyl ligands found in lanthanide complexes

lanthanide alkyl species [189]. The first studies directed towards the synthesis of homoleptic systems proved to be unsuccessful, probably due to an unfavorable strategy of synthesis [131]. However, intramolecular donor-stabilization was structurally confirmed in heteroleptic complexes of type $Cp^{\ddagger}_2$ Ln(alkyl) [190]. Allylic moieties are also very effective in stabilizing low aggregated organolanthanide species as confirmed in mononuclear homoleptic phosphinomethanide, benzamidinate [32] and azaallyl complexes [164].

The efficiency of functionalized cyclopentadienyl complexes is meanwhile well established [78, 191–202]. Because cyclopentadienyl ligands still dominate the field of organolanthanide chemistry, a selection of the functionalized ligands utilized is depicted in Fig. 11. In the field of aryl complexes, which represented the first well-characterized homoleptic derivatives [203], multiple functionalization has already been started [204].

5 Conclusion

The lanthanide series is the largest subgroup in the periodic table offering a unique, gradual variation of electronic and steric characteristics. Rare earth cations appear to be an "extended playground of Lewis acidity, electrophilicity, oxophilicity, and redoxstability" to organic substrates. The large cations, give rise to complex geometries, which are capable of accommodating highly sophisticated ligands, which in turn typically direct the complex reactivity. The considerably ionic nature of organolanthanide compounds not only produces unexpected and exciting coordination chemistry but also permits the rapid ligand exchange and insertion reactions that govern catalytic transformations. Thermally stable and tailor-made molecular precursors are also desirable in processes such as MOCVD. Thin films of advanced materials, characterized by the optical, magnetic and electronic properties of binary or ternary lanthanide composites, are required, for example, in permanent magnets, magneto-optic records, electro-optic displays, dielectric condensators, doped semiconductor materials, high-temperature superconductors, light-emitting electrodes, etc. [205].

The text of this chapter on "Features of Organolanthanide Chemistry" has been geared to the precursor chemistry of potential applications in the fields of catalysis and material sciences, which are certainly two of the most-discussed topics in current publications. However, organolanthanide chemistry has also penetrated other important areas: for example, in a text on macrocyclic derivatives the topic "probes in life" is to be found [92].

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Lanthanide Amides

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Table of Contents

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List of Symbols and Abbreviations

A	adduct ligand
ac	acetonate
acac	acetylacetonate
AIP	2-phenylamino-4-phenylimino-2-pentene
bdsa	bis(dimethylsilyl)amide

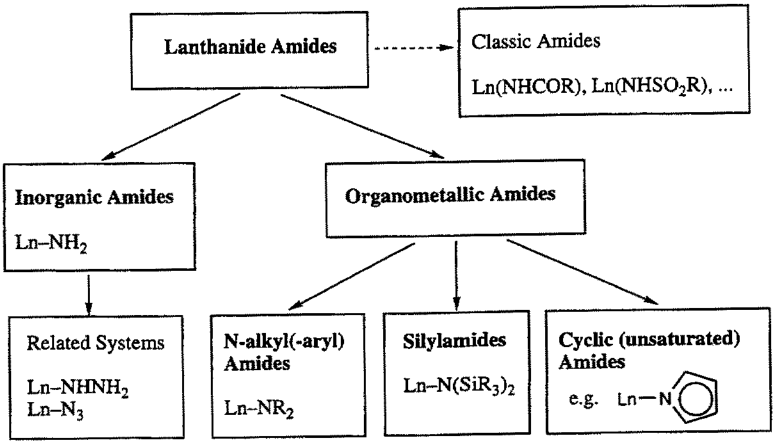
BiPy	bipyridine
btsa	bis(trimethylsilyl)amide
cbz	carbazole
COT	cyclooctatetraene
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
DAB	1,4-diazabutadiene
H_2-DAC	4,13-diaza-18-crown-6
DME	1,2-dimethoxyethane
dmp	dimethylpyrrole
DMPE	1,2-bis(dimethylphosphino)ethane
dmpz	dimethylpyrazole
Im	imidazole
L	ligand
Ln	lanthanide (Sc, Y, La, Ce–Lu)
Nc	naphthalocyanine
OEP	2,3,7,8,12,13,17,18-octa(ethyl)porphyrin
OEPG	*meso*-octaethylporphyrinogen
p	pyrrole
Pc	phthalocyanine
pin	2-phenylindole
Por	porphyrin
Py	pyridine
pz	pyrazole
silox	tri-*tert*-butyl siloxide
TCB	1,2,4-trichlorobenzene
thd	2,2,6,6-tetramethyl-3,5-heptanedionate
THF	tetrahydrofurane
TPP	*meso*-tetra(phenyl)porphyrin
tritox	tri-*tert*-butyl methoxide
trop	tropolonate
TTP	*meso*-tetra(tolyl)porphyrin

The present review should be seen far beyond pure homage to organometallic lanthanide amide chemistry. The class which is settled between the alkyl and alkoxide counterparts has claimed its own importance within the family of organolanthanide compounds during the last ten years. Meanwhile compound design can fall back on an extensive reservoir of sterically and electronically tailored ligands. Of course, the "lanthanide dilemma" requires special emphasis on structural chemistry, although, encouraging applications should highlight this review. The thermal stability and kinetic lability of the Ln–N bond make this class of lanthanide compounds not only a valuable synthetic precursor. The article covers the literature until mid-1995 and seeks to uncover the current trends in this field.

1 Introduction

Historical Sketch. The first organometallic transition metal amide, $Zn(NEt_2)_2$, was synthesized in 1856 by Frankland [1]. Corresponding chemistry of the early transition metals started relatively late when Dermer and Fernelius obtained $Ti(NPh_2)_4$ in 1935 [2]. Another 20 years later the synthesis of the first *f*-transition metal amide $U(NEt_2)_4$ was reported (Jones et al. 1956 [3]). The first molecular lanthanide amide complex appeared in 1963 (Maginn et al.) in the form of "Cp_2ErNH_2" [4]. Shortly after that lanthanide phthalocyanines (Kirin et al. 1965 [5]) and the inorganic amide $La(NH_2)_3$ (Juza et al. 1966 [6]) were synthesized. In the early 1970s Bradley et al. started detailed investigations of homoleptic low molecular amide derivatives by means of the bulky ligands bis(trimethylsilyl)amide [7] and bis(isopropyl)amide [8].

The historical sketch outlines the class of lanthanide amides this article is to deal with and which is further manifested in Scheme 1. Organometallic amides which can be classified as dialkyl (-aryl, -silyl) amides and amides derived from unsaturated heterocyclic ligands are seen with respect to N-unsubstituted (primary, inorganic) amides. The consideration of more classic coordination compounds like acid amides or sulfonamides, often ascribed as "wet chemistry", is excluded. The historical data also demonstrate the relatively late start of lanthanide amide chemistry reflecting the late industrial establishment of the lanthanide elements (separation, purification, etc.) [9]. However, lanthanide amides are still the youngest class in conjunction with the most important pillars of organometallic lanthanide chemistry, namely the alkyls/cyclopentadienyls ($LnCp_3$, 1954, [10]) and the alkoxides "$(Ce(OR)_4$", 1956 [11a]; "$La(OR)_3$", 1958 [11b]). Indeed most of the work has been conducted in the last ten years.



Scheme 1. Classification of lanthanide amides

"Metal dialkylamides $M(NR_2)_x$ . . . are of special interest in that they . . . . occupy a position between the metal alkoxides and the metal alkyls" [12]. This meaningful statement of Bradley will often be referred to later, when interrelations between these three fundamental classes of compounds are discussed. Amide ligands like alkoxide ligands are hard ligands (Pearson) and prefer hard metal centers. Thus lanthanide metals represent optimal targets and the resulting synergism often leads to thermally stable and sublimable compounds, whereas the alkyl derivatives are normally thermally labile. In addition, amide ligands face the problem "steric saturation of lanthanide centers" by increased steric and structural flexibility in comparison to alkoxide ligands: three bond separation vs two bond separation (Fig. 1). That means the shielding of both the lanthanide center and the Ln–N bond can occur more effectively by two substituents in β-position to the lanthanide metal.

As a consequence monomeric complexes are obtained much more easily. Also, the tendency to bridge lanthanide centers is less distinct and, for example, a "small cluster" chemistry as it exists for alkoxides, e.g. O*i*Pr [13] and O*t*Bu derivatives [14], is not yet known. However, the Ln–N(amide) bond is less strong than the Ln–O(alkoxide) bond, and even comparable to Ln–C(alkyl) bonds, which has an effect in synthetic chemistry. This has been confirmed by the determination of absolute bond disruption enthalpies D by means of calorimetric titrations for the representative systems Cp*Sm–X (X = O*t*Bu, D = 82.4 kcal mol^{-1}; NMe_2, 48.2; $CH(SiMe_3)_2$, 47.0) [15].

During the last five years lanthanide amides, and in particular the silylamides, have attracted considerable attention under the assumed name "precursors for electronic and ceramic materials" [16, 17]. Herein the systems $Ln[N(SiMe_3)_2]_3$, for their part, provide essential precursors for the generation of, e.g., pure alkoxides. However, while the steric environment of the alkoxide ligand declined excessively [18], variation of the amide ligand seemed to stick. This goes hand in hand with the very recent start of the exploration of organometallic lanthanide amides themselves as molecular precursors to, e.g., lanthanide metals or lanthanide nitrides (Sect. 7.2).

On the other hand, the specific electron configuration of the nitrogen allows a chemistry comparable to that of the ubiquitous cyclopentadienyl ligand and this offers an opportunity to get within distance of the all-powerful lanthanide alkoxide chemistry. The introduction of unsaturated monoanionic ligands like substituted pyrrols is currently in progress. In the last ten years there has also been a steadily growing interest in polycyclic amides, e.g., porphyrins and phthalocyanines.

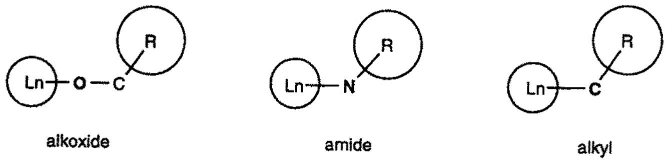
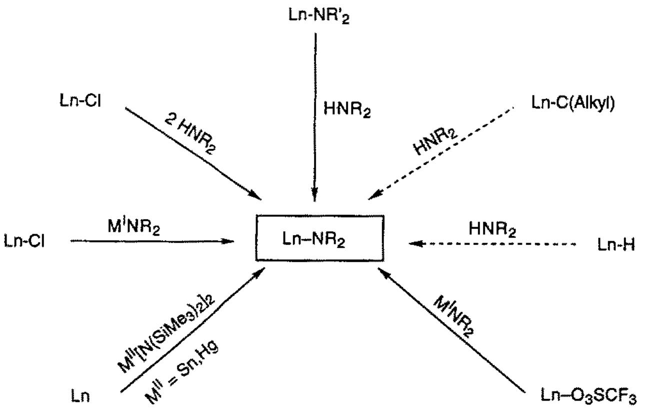


Fig. 1. Three bond separation vs two bond separation



Scheme 2. Generation of Ln–N amide bonds

Synthetic Sketch. Scheme 2 indicates common synthetic routes to Ln–N(amide) bonds. Important syntheses differing from this which are compound specific are mentioned in the article.

The present article will focus in particular on structurally characterized complexes and will refer to current trends and potential applications, simultaneously aiming at a coherent picture of the entire family of organometallic lanthanide amides including the inorganic derivatives. The elements Sc, Y, La will be treated as lanthanide elements Ln. Previous reviews cover this subject mostly as an aspect wrapped up under a comprehensive depiction of both "metal amides" [19] and "lanthanide chemistry" [20]. Other articles focus on special topics in this field, e.g., inorganic amides [21], silylamides [22], phthalocyanines [23] or porphyrins [24].

2 N-Unsubstituted Amides – Derivatives of Ammonia

NH_2^- NH^{2-} $NHNH_2^-$ $NHNH^{2-}$ N_2^{2-} N_2^{4-} N_3^-

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From the viewpoint of molecular chemists, "inorganic metal amides" or primary amides, the derivatives of ammonia, are related to solid state chemistry. However, both inorganic and organometallic amides are mentioned in the same breath. In a world of new materials where, e.g., ceramics [16, 17] and hard coatings [25] are obtained by means of molecular precursors, the organometallically orientated chemist has to deal with classic solid state compounds. Accordingly the beginning and end of lanthanide amide chemistry is ascribed to the lanthanide nitrides [26–32]. Binary nitrides LnN are refractory materials (mp 2400–2900 °C) with extraordinary physical properties. The bonding is described as roughly 50% ionic and does not show the structural variety of the predominantly covalent higher pnictides [27a]. LnN possess a cubic face-centered NaCl-type structure (Fm3m) [30], frequently suffering from instoichiometries (LnN_{1-x}) [26, 27]. Higher nitrides can be obtained from the metals at increased nitrogen pressure (30–300 atm). The early elements Ce, Pr, Nd form hexagonal dinitrides LnN_2, whereas the late elements Y–Lu yield instoichiometric mixtures of LnN and LnN_{1+x} (cubic, $x = 1.2 \ldots 1.4$) [31]. Lanthanide nitrides are moisture sensitive and decompose to oxide hydroxides when exposed to air.

A common precursor to LnN are the simple inorganic amides $Ln(NH_2)_x$ ($x = 2, 3$) which can be placed between the nitrides and the alkyl substituted amides. Their main use lies in the synthesis of other solid materials like lanthanide hydroxides [21, 33], carbides [34] or above-mentioned nitrides. Very recently solutions of europium and ytterbium in liquid ammonia have been rediscovered as synthetic tools (Sect. 7.1).

2.1 Homoleptic Complexes [35]

In 1956 it was found that europium and ytterbium dissolve in liquid ammonia with the characteristic deep blue color known for the alkali and alkaline earth metals [36–40]. This behavior arises from the low density and high volatility of those metals compared to the other lanthanide elements [41]. Samarium, which normally also occurs in the divalent oxidation state, does not dissolve under identical conditions [37].

$$Ln + mNH_3(liq) \rightarrow Ln^{2+}(NH_3)_6 \cdot 2e^-(NH_3)_n \tag{1a}$$

$$e^-(NH_3)_n + NH_3 \rightarrow NH_2^- + 0.5H_2 + nNH_3 \tag{1b}$$

$$Ln^{2+} + 2NH_2^- \rightarrow Ln(NH_2)_2 \quad (Ln = Eu, Yb) \tag{1c}$$

$$Yb(NH_2)_2 + NH_2^- + n(NH_3) \rightarrow Yb(NH_2)_3 + e^-(NH_3)_n \tag{1d}$$

$$Ln(NH_2)_2 \xrightarrow{\Delta} LnN + NH_3 + 0.5H_2 \quad (Ln = Eu, Yb) \tag{1e}$$

$$Eu(NH_2)_2 \xrightarrow{\Delta} EuNH + NH_3 \tag{1f}$$

The initially formed ammoniates $Ln(NH_3)_6$ (Eq. 1a) can be isolated by evaporation of NH_3 as gold metallic solids and low temperature X-ray studies at 200 K reveal a body-centered cubic array of octahedral molecules [38a]. $Eu(NH_3)_6$ can easily be converted to pure $Eu(NH_2)_2$ by catalytical (Fe_2O_3) [40a] and thermal (50 °C) treatment [40b] (Eq. 1b, c). In the case of ytterbium a mixture of $Yb(NH_2)_2$ and $Yb(NH_2)_3$ is obtained due to the reducing power of Yb(II) (Eq. 1d) [40c]. Formation of $Yb(NH_2)_3$ could be reduced by thermal decomposition at lower temperature [40d]. Pure $Yb(NH_2)_2$ can be synthesized by avoiding the liquid phase and reaction of Yb metal with gaseous ammonia at 3 atm pressure [42]. Thermal degradation of the binary amides finally yields LnN according to Eq. (1e). The first decomposition step of the $Eu(NH_2)_2$ degradation (230 °C) gave rise to imide formation, EuNH, where the metal is still divalent (Eq. 1f) [40c].

Application of the ammonothermal synthesis [6] allowed the isolation of more crystalline materials and access to trivalent species. The process requires ammonia in supercritical region up to 5000 atm and 550 °C and reaction periods in the range of 5–50 days. The structures and properties of $Ln(NH_2)_2$ (Ln = Eu, Yb [43]) and $Ln(NH_2)_3$ (Ln=La [44], Sm [45], Y [46], Yb [43]) have been examined. Single crystals of $La(NH_2)_3$ were obtained by a chemical transport reaction with KNH_2 as a mineralizer (Eq. 2). The presence of alkaline metal as a mineralizing agent during recrystallization hampered the isolation of pure $Ln(NH_2)_3$. Ternary systems of type $M[Ln(NH_2)_4]$ and $M_3[Ln(NH_2)_6]$ have proven to be favoured crystallization products. Derivatives of the late lanthanide elements proved to be less stable due to their increased charge density. The preferred formation of ternary or *ate* (organometallic) systems will run as a central theme through this article. $Eu(NH_2)_2$ crystallizes as anatas-type with two Eu–N distances of 2.59(4) and four of 2.730(2) Å [43]. The bond lengths in 6-coordinated organometallic complexes $Eu[N(SiMe_3)_2]_2(DME)_2$ (2.530(4) Å) and $Eu(cbz)_2(THF)_4$ (2.545(5), 2.572(5) Å, Sects. 4.2.2 and 6.1) are very close.

$$2La(NH_2)_3 + KNH_2 \rightleftharpoons KLa_2(NH_2)_7 \qquad (2)$$

The binary Ln(III) amides show three different solid structures for La, Sm and Y/Yb according to their powder diffraction pattern. The crystal structure of $La(NH_2)_3$ has been examined in more detail and turned out to be very complicated (Fig. 2). Two crystallographically independent lanthanum cations are building up double layers and are connected within the layers through NH_2^- ions. Each La is surrounded by eight amide anions and the La–N distances range from 2.52 to 2.95 Å. The average values are 2.74 Å for La(1) and 2.67 Å for La(2). The geometries around La can be described as distorted square antiprismatic (La(1)) and distorted trigonal prismatic with one anion above a rectangular plane and one anion completing a triangular to a rectangular plane (La(2)).

The ternary systems display a variety of structural chemistry depending on the sizes of the alkaline and lanthanide metals (Scheme 3; Fig. 3 [43, 45–57]). The smaller alkali cations determine the expected coordination structures as found in salt-like compounds, e.g., $Na_3Y(NH_2)_6$ or $KY(NH_2)_4$. Layer structures are observed in alkali metal poor systems like $MLa_2(NH_2)_7$ while cesium derivatives, apart from the lanthanum compounds, form perowskit-like arrangements as in $CsEu(NH_2)_3$ and $Cs_3Ln_2(NH_2)_9$. The mono ammoniates of some Cs-systems are probably metastable. Preparation of analogous ternary systems with Li were unsuccessful in contrast to, e.g., $LiAl(NH_2)_4$ [58].

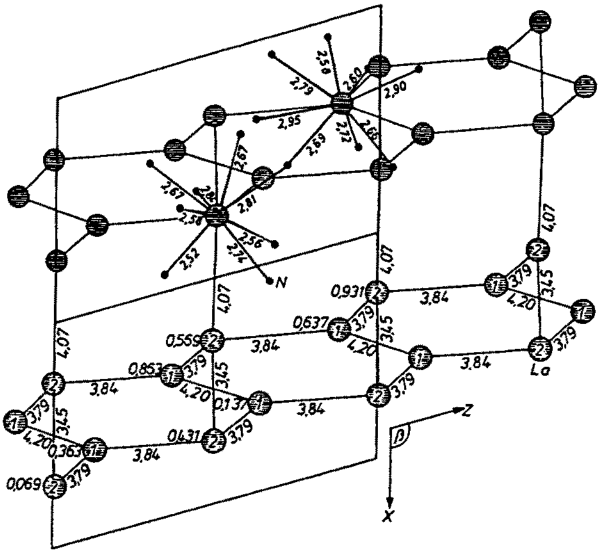


Fig. 2. Projection of the La^{3+} arrangement in $La(NH_2)_3$ along with La–La and La–N bond distances (Å) [44a]

	$KLn_2(NH_2)_7$ *Pnnm* Ln = La, Ce, Sm [45, 49]	$RbLn_2(NH_2)_7$ [21a]	$CsLa_2(NH_2)_7$ *Pbca* [55]
$Na_2Eu_3(NH_2)_8$ *Fddd* [43c]	$KEu(NH_2)_3$ *Fddd* [43b]	$RbEu(NH_2)_3$ *Fddd* [53]	$CsEu(NH_2)_3$ [21a] $Cs_3Ln_2(NH_2)_9$ $R\bar{3}c$ Ln = Ce, Nd, Sm, Y, Yb [56]
$NaLn(NH_2)_4$ $P2/n2/n2/n$ Ln = Gd, Y, Yb [46, 47]	$KLn(NH_2)_4$ $C2/c$ Ln = Y, Yb [50]	$RbLn(NH_2)_4$ $P\bar{1}$ Ln = Y, Yb [50]	$Cs_3Ln_2(NH_2)_9$ $P6_3/mmc$ Ln = Nd, Gd [56]
$Na_3Ln(NH_2)_6$ *Fddd* Ln = La, Gd, Y [46–48a]	$K_3Ln(NH_2)_6$ $C2/m$ Ln = La, Ce, Sm, Eu [43b, 45, 49, 51]	$Rb_3La(NH_2)_6$ $R\bar{3}c$ [54]	$Cs_3Ce_2(NH_2)_9$ $P3$ [56]
$Na_3Yb(NH_2)_6$ *Pbca* [48b]	$K_3Ln(NH_2)_6$ $R32$ Ln = Y, Yb [52]	$Rb_3Ln(NH_2)_6$ $R32$ Ln = Nd, Eu, Y [52, 54] $Rb_3Yb(NH_2)_6$ $P2_1/n$ [52]	$Cs_3La(NH_3)_6 \cdot NH_3$ $P2_1/n$ [57] $Cs_4La(NH_3)_7 \cdot NH_3$ $P2_1/c$ [57]

Scheme 3. Structural trends in ternary "$M_xLn_y(NH_2)_z$"

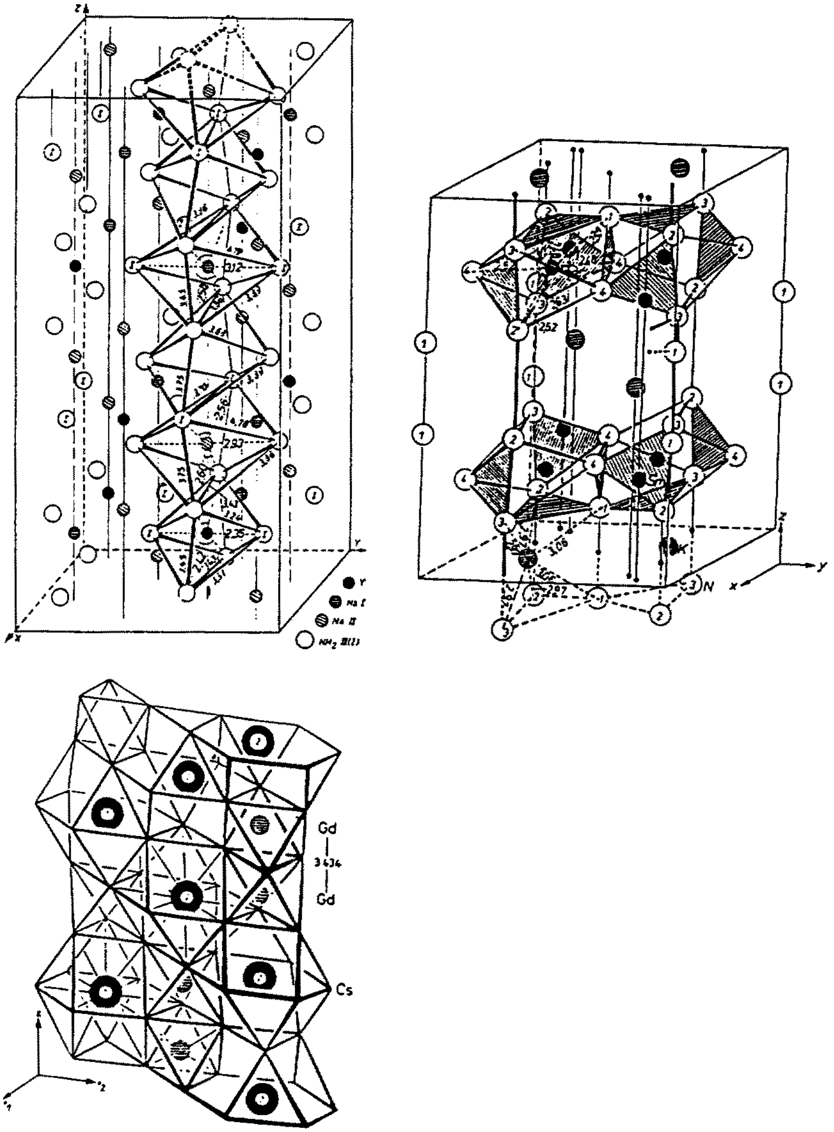


Fig. 3. Structural trends in ternary "$M_xLn_y(NH_2)_z$" represented by details of the solid state structures of $Na_3[Y(NH_2)_6]$ ("salt") [46], $KSm_2(NH_2)_7$ ("layer") [45] and $Cs_3Gd_2(NH_2)_9$ ("perowskit") [56b]

Microcrystalline imides, e.g., $La_{0.666}NH$ [44b] and imide-nitrides, e.g., $Ce_3(NH)_3N$ [49b] were obtained by thermal decomposition of amide precursors.

What is the message of these inorganic metal amides? As hydroxides are never classified to alkoxides, NH_2 amides seem to be treated separately from the organometallic amides. However, methanides are always mentioned in the same breath with complexes containing branched or otherwise substituted alkyls. "Bradley's statement" might be even translatable to systems derived from the smallest ligands OH, NH_2, CH_3. And already, at second glance, there is some validity for this. Like lanthanide methanides, $Ln(NH_2)_x$ ($x = 2, 3$) are sensitive to moisture to yield $Ln(OH)_3$. While $Ln(OH)_3$ can be readily synthesized [33], isolation of pure $Ln(NH_2)_3$ is complicated and the system "$Ln(CH_3)_3$" still awaits characterization. Unlike the hydroxides, $Ln(NH_2)_3$ do not show a simple solid state structure due to both the enhanced ability of polarization and the size and geometry of the NH_2^- anion. Lanthanide methanide complexes have been fully defined in form of Li-*ate* complexes of type $[Li(solvent)]_3[Ln(CH_3)_6]$ [59] or as aluminate $Ln[AlMe_4]_3$ and gallate $Ln[GaMe_4]_3$ complexes, respectively [60]. The influence of the alkali metal M on the stabilization of ternary $M/Ln/NH_2$ compositions was thoroughly studied, but, their impact in "CH_3" chemistry is unknown. Like lanthanide alkyls the solutions of europium and ytterbium in ammonia are accessible to plenty of bond transformations (Sect. 7.1). Simple ligands like NH_2^- represent more complicated molecules in computational calculations [61].

2.2 Heteroleptic Complexes

Compounds of type $[Cp_2LnNH_2]_2$ were obtained by simple metathesis reaction or by thermal decomposition (200–250 °C) of complexes $Cp_3Ln(NH_3)$ according to Eq. (3) [4, 62]. Both the ammonia (150–160 °C, for the smaller lanthanides) and the heteroleptic amide complexes (230 °C) can be sublimed under high vacuum. The Ce(IV) amide derivatives Cp_3CeNH_2 and $Ind_2Ce(NH_2)_2$ were also discussed as metathesis products.

$$2Cp_2LnCl + 2NaNH_2 \rightarrow [Cp_2LnNH_2]_2 + 2NaCl \qquad (3a)$$

$$2YbCp_3 + 2NH_{3\,liq} \rightarrow 2Cp_3Yb(NH_3) \rightarrow [Cp_2YbNH_2]_2 + 2C_6H_6 \qquad (3b)$$

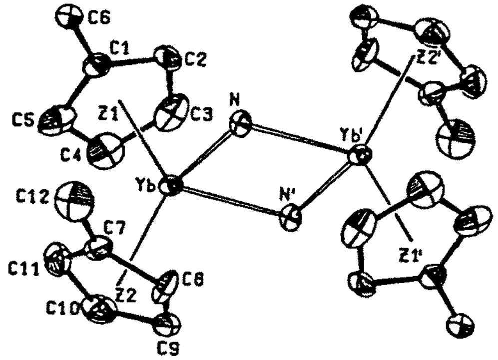


Fig. 4. ORTEP view of $[Yb(MeCp)_2(\mu\text{-}NH_2)]_2$ [63]

$[Yb(MeCp)_2(\mu\text{-}NH_2)]_2$, obtained as a byproduct in the Yb/NH$_3$liq/MeCpH-system was structurally characterized [63]. A view of the dimeric molecule is shown in Fig. 4. The Yb–N bond lengths are 2.29(1) and 2.32(1) Å, respectively. Comparable distances were found in 6-coordinated ternary systems $NaYb(NH_2)_4$ (2.28(2)–2.44(2) Å) [47] and $Na_3Yb(NH_2)_6$ (2.32(7)–2.42(7) Å) [48b]. The Yb–Yb distances are 3.53(1) Å in $[Yb(MeCp)_2(\mu\text{-}NH_2)]_2$ and 3.70 Å in $NaYb(NH_2)_4$, respectively.

2.3 Related Species

2.3.1 Hydrazides

The observation that nitrogen interacts with the strongly reducing organometallic complex $SmCp^*_2$ to form $[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$ [64] led to the investigation of the reaction behavior of other substrates containing a N–N linkage like hydrazines (Table 1). $[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-HNNH})$ is formed in the reaction of both $SmCp^*_2$ and $[Cp^*_2Sm(\mu\text{-}H)]_2$ with N_2H_4 under release of hydrogen [65]. An interesting reaction occurred by treatment of the THF adduct of $[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-HNNH})$ with $(Et_3NH)BPh_4$ [65]. The molecular structure of the resulting complex (Fig. 5) reveals a rare example of protonation of a metal coordinated N_2H_2 unit to hydrazine. This is remarkable in so far as subsequent protonation of metal coordinated N_2 to NH_3 is one model for dinitrogen fixation in biological systems [65]. The redox stability of Sm(III) is an important factor for the isolation of such complexes. Reaction of $SmCp^*_2$ with excess hydrazine yielded a tetranuclear molecule containing differently charged hydrazide anions, namely $(NH_2NH)^-$ and $(NHNH)^{2-}$ [66].

The scandium hydrazido linkage of $Cp^*_2Sc(NHNR_2)$ (R = H, Me) inserts acetonitrile to form heterometallacycles (Scheme 4) [67]. The resulting shorter Sc–N contacts of 2.155(4) and 2.161(4) Å, respectively, were ascribed to the

Table 1. Lanthanide complexes relevant to the modelling of dinitrogen fixation

Complex	Type of N-fragment	Ln–N [Å]	Ref.
$[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-}N_2)$	N_2^{2-}	2.347(6), 2.368(6)	[64]
$[Cp^*Sm]_4(NHNH)_2(NHNH_2)_4(NH_3)$	NH_3	2.66(1)	[66]
	$NHNH^{2-}$	2.437(9)–2.629(9)	
	$NHNH_2^-$	2.432(9)–2.51(1)	
$[Cp^*_2Sm(THF)]_2(\mu\text{-}\eta^2:\eta^2\text{-HNNH})$	$N_2H_2^{2-}$	2.413(4)–2.459(4)	[65]
$[Cp^*_2Sm]_2(\mu\text{-}\eta^2:\eta^2\text{-HNNH})$	$N_2H_2^{2-}$	2.313(4), 2.436(4)	[65]
$[Cp^*_2Sm(THF)(\eta^2\text{-}N_2H_4)][BPh_4]$	N_2H_4	2.492(2), 2.523(2)	[65]
$[(THF)_2Li(OEPG)Sm]_2(N_2Li_4)$	N_2^{4-}	2.342(2), 2.357(2)	[68]
$Cp^*_2Yb(NH_3)(THF)$	NH_3	2.55(3)	[69]
$Cp^*_2Yb(TePh)(NH_3)$	NH_3	2.50(1)	[70]
$(iPrCp)_3Er(NH_3)$	NH_3	2.457(5)	[71]

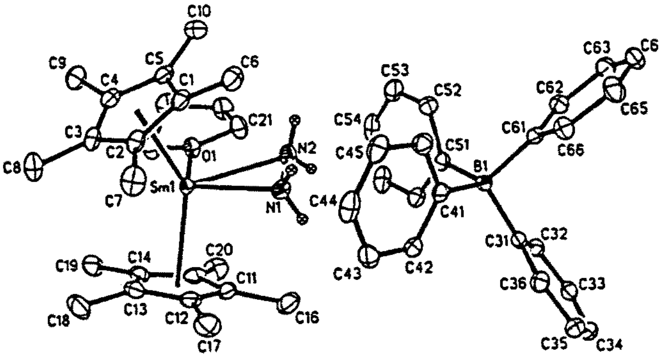
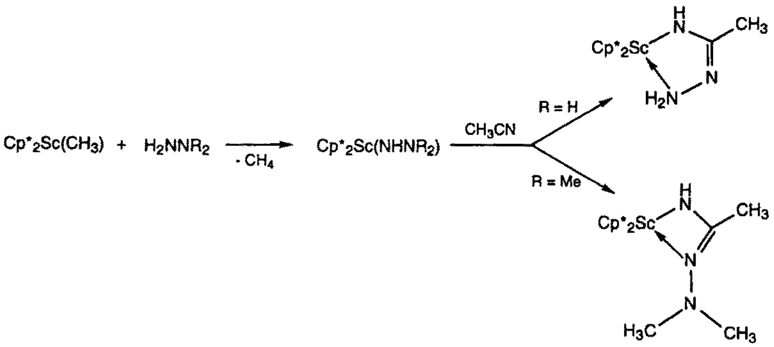


Fig. 5. Crystal structure of $[\mathrm{Cp}^*_2\mathrm{Sm}(\eta^2\text{-}\mathrm{H_2NNH_2})(\mathrm{THF})][\mathrm{BPh_4}]$ [65]



Scheme 4. Acetonitrile insertion into scandium hydrazido moieties

acetonitrile nitrogen by ^{15}N-labelling experiments. The steric bulk of the dimethylamino group most likely caused the smaller ring size.

Encapsulation of N_2 into a $\mathrm{Sm}_2^{\mathrm{III}}\mathrm{Li}_4$ metallic cage was found following the reaction sequence expressed in Eq. (4) [67]. A “green Sm(II) compound” is most likely part of the formal reduction of N_2 to N_2^{4-}. Table 1 summarizes some structurally characterized complexes with relevance to this subject.

$$\mathrm{SmCl_3(THF)_3} + \mathrm{(OEPG)Li(THF)_4} \xrightarrow{\mathrm{Li(Ar)}} \text{“green crystals”}$$

$$\xrightarrow{N_2} \mathrm{[(THF)_2Li(OEPG)Sm]_2(N_2Li_4)} \quad (4)$$

2.3.2 Azides

Typical reaction conditions for the formation of lanthanide azides are described in Eq. (5) [72–73]. Like other heavy metal azides, lanthanide azides can be explosive under grinding and heating. Different reaction behavior compared to lanthanide amides is expressed both in their synthesis and stability in aqueous systems. Conspicuous again is the preferred formation and stabilizing effect, respectively, of *ate* complexation.

$$2Nd(OH)_3 + H_2NC_2H_4NH_2 + 8HN_{3_{gas}} \rightarrow [C_2N_2H_{10}]^{2+}[Nd_2(N_3)_8]^{2-} + 6H_2O \qquad (5a)$$

$$10CsN_3 + Eu_2O_3 + 6HN_{3_{gas}} \rightarrow 2Cs_5Eu(N_3)_8 + 3H_2O \qquad (5b)$$

The structurally characterized lanthanide azides show a remarkable variety of structures. There have been found 3-dimensional networks of $Nd(N_3)_8$ polyeders in $[C_2N_2H_{10}][Nd_2(N_3)_8]$ (Nd–N, 2.470(7)–2.657(6) Å) [72a] and $Cs_2Nd(N_3)_5$ (Nd–N, 2.45(3)–2.64(3) Å) [73a], 2-dimensional layer structures in $Cs_3La(N_3)_6$ (2.55(3)–2.79(3) Å) [73b] and $Cs_3[Nd_2(N_3)_9(H_2O)_2]$ (2.46(1)–2.57(1) Å) [72b] and isolated $Eu(N_3)_8$ antiprisms where all N_3^- ligands are terminal with respect to the lanthanide center (2.44(2)–2.57(2) Å) [73c]. The observed coordination numbers of the lanthanide cations are eight or nine.

An organometallic azide complex was obtained by replacement of THF through the azide anion in $Cp_3Sm(THF)$ (Eq. 6) [74]. The molecular structure exhibits different and comparatively large Sm–N–N angles of 134(1) and 151(1)°. The Sm–N bond lengths of 2.47(2) and 2.48(2) Å are comparable to those of the inorganic azides.

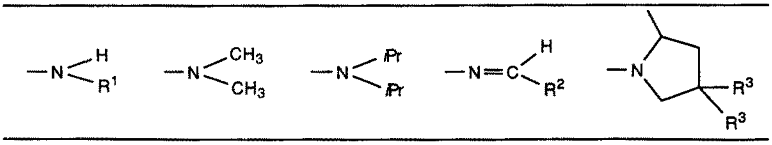
$$2Cp_3Sm(THF) + LiN_3 \xrightarrow{DME} [Li(DME)][Cp_3Sm{-}N_3{-}SmCp_3] \qquad (6)$$

3 Complexes with Simple N-Substituted Ligands

Lanthanide chemistry is dominated by large, anionic ligands which meet the steric and electronic demands of these large electropositive metals. Therefore it is not surprising that the chemistry of simple homoleptic organometallic amides is poorly developed. In particular, characterization of homoleptic compounds $Ln(NMe_2)_3$, $Ln(NEt_2)_3$ or $Ln(NHPh)_3$ has never appeared in the literature and homoleptic alkoxide (methoxide, ethoxide) [11b, 75] and alkyl (methyl, ethyl) [59] counterparts tend to be either insoluble or unstable. This is even more surprising because the NEt_2 ligand is sterically more demanding than well examined O*i*Pr and O*t*Bu ligands [75]. Consequently homoleptic Uranium(IV)diethylamide was found to be only dimeric in the solid state [76].

A few heteroleptic complexes have been isolated in the presence of bulky deoligomerizing ligands [15, 77, 78], e.g., $Cp^{\ddagger}_2La(NHCH_3)(H_2NCH_3)$ [77] or $Cp^{\ddagger}_2Sm(HNPh)$ [65b].

3.1 Alkyl-Substituted Ligands



R^1 = Me, Et, tBu; R^2 = Me, tBu; R^3 = H, Me

Very recently a method was described for the isolation of soluble complexes of such small amide ligands [60]. Insoluble systems, formed by the reaction of anhydrous $LnCl_3$ with three equivalents of $LiNMe_2$ in THF, were cracked under mild conditions (room temperature) by the attack of strong, soluble Lewis acids to form alkane-soluble tractable compounds of type $Ln(NMe_2)_3(MMe_3)_3$ (Eq. 7; M = Al, Ga; Table 2). The molecular structure, as shown, of the Sm/Ga derivative in Fig. 6 reveals a two-fold symmetry. Two symmetrically identical $[(\mu\text{-}NMe_2)(\mu\text{-}Me)MMe_2]$ chelating units form Ln–C(Me) contacts of 2.749(7) Å. The third NMe_2MMe_3 unit involving N(2) is disordered about a two-fold symmetry axis and displays rather a non-chelating character (Ln–C 3.28 Å).

$$LnCl_3 + 3LiNMe_2 \longrightarrow Ln(NMe_2)_3(LiCl)_3 \xrightarrow[-3LiCl]{3MMe_3} Ln(NMe_2)_3(MMe_3)_3 \qquad (7)$$

$$La(NMe_2)_3(LiCl)_3 \xrightarrow[-3LiCl]{4GaMe_3} La(Me)(NMe_2)_2(GaMe_3)_3 + 0.5[Me_2NGaMe_2]_2 \qquad (8)$$

Table 2. Complexes derived from simple amide ligands

Compound	Ln–N [Å]	CN[a]	Ref.
$Cp^*_2La(NHMe)(H_2NMe)$	2.323(10)	8	[77]
$Nd(NMe_2)_3(AlMe_3)_3$	2.435(4), 2.433(8)	5(7)	[60a]
$Nd(NMe_2)_3(GaMe_3)_3$	2.395(5), 2.362(1)	5(7)	[60a]
$Sm(NMe_2)_3(GaMe_3)_3$	2.357(4), 2.355(8)	5(7)	[89]
$La(NMe_2)_2Me(GaMe_3)_3$	2.451(4), 2.444(4)	6	[60a]
$LiNd(NiPr_2)_2(\mu\text{-}NiPr_2)_2(THF)$	2.291(2), 2.83(17), 2.393(15), 2.406(16)	4(8)	[82]
$LiLa(NiPr_2)_2[\mu\text{-}P(C_6H_4OMe\text{-}o)_2]_2(THF)$	2.30(1)	6(8)	[79]
$Nd(NiPr_2)_2Me(AlMe_3)_2$	2.167(2), 2.508(2)	5(6)	[82]
$[Cp_2Y(N{=}CHtBu)]_2$	2.314(9), 2.382(9)	7	[86]
$[Cp_2Y(HC{=}NtBu)]_2$	2.325(4)	9	[87]
$[Cp_2Er(HC{=}NtBu)]_2$	2.296(5), 2.312(5)	9	[87]

[a] Values in parenthesis add all close Ln···C contacts as a full coordination number

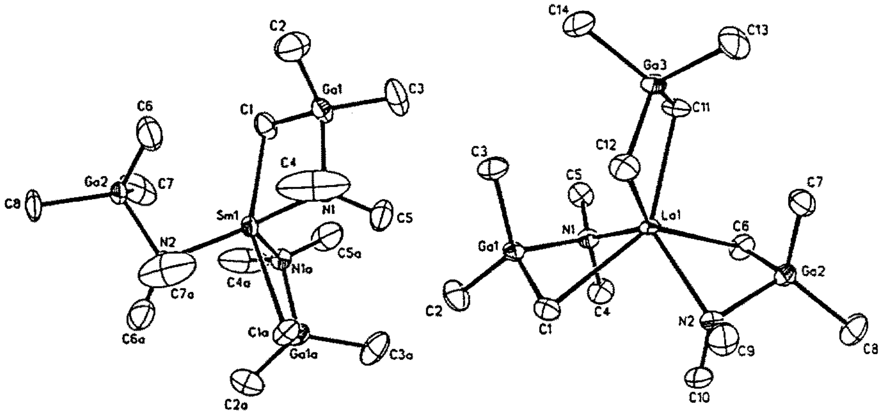


Fig. 6. Molecular structure of compounds $Sm(NMe_2)_3(GaMe_3)_3$ [89] and $La(Me)(NMe_2)_2(GaMe_3)_3$ [60a]

Partially methyl exchanged complex $La[(\mu\text{-}Me)_2GaMe_2][(\mu\text{-}Me)(\mu\text{-}NMe_2)GaMe_2]_2$ was obtained by examination of the analogous lanthanum system with four equivalents of $GaMe_3$ (Eq. 8, Fig. 6, Table 2). A characteristic feature of the resulting molecular structure are rather long La–C(Me) contacts. The La–C distances in the two heteroleptic bridging units even resemble agostic interations (av 2.942(5) Å). Consequently, reaction of mixture $Ln(NMe_2)_3/LiCl$ with excess of MMe_3 yielded the permethylated alanate and gallate complexes $Ln(MMe_4)_3$ (Sect. 7.1).

Even reports on amide complexes of the sterically bulkier $NiPr_2$ ligand are limited [8, 79–82], in spite of the readily available precursor $LiNiPr_2$ (LDA) [83]. Though the systems $Ln(NiPr_2)_3(THF)$ were described almost 20 years ago [8], they, unlike the $Ln[N(SiMe_3)_2]_3$ derivatives, never received that attention. Possible reasons might be their enhanced chemical and thermal instability (even that of their alkali precursor [83]), lack of structural characterization and presence of coordinated solvent. In addition the synthesis of $Ln(NiPr_2)_3(THF)$ is hampered by the formation of hexane soluble ate complexes $Li(THF)Ln(NiPr_2)_4$, (Ln = La, Nd, Y, Yb) [81, 82] of which the neodymium derivative has been fully defined by X-ray crystallography (Fig. 7, Table 2) [82]. The yttrium and ytterbium derivatives were shown to be isostructural [81]. Lanthanide *ate* complexes are often both favored coproducts and crystallization products [84]. However, pure $Ln(NiPr_2)_3(THF)$ could be obtained by reaction of $LnCl_3$ with 2.5 equivalents of $LiNiPr_2$ [81]. Therefore the system "$Ln(NiPr_2)_3$" still claims to be a potential competitor to the dominating $Ln[N(SiMe_3)_2]_3$ and gained recent interest (Sect. 7.1).

Unique reaction behavior of the ligand fragment $NiPr_2$ is obvious when $Ln(NiPr_2)_3(THF)$ is treated with $AlMe_3$ [82]. A complex could be isolated with a set of three different ligands (Fig. 7, Table 2): a terminal $NiPr_2$-ligand is formally unchanged from the starting material, a "transition" $[(\mu\text{-}NiPr_2)(\mu\text{-}Me)AlMe_2]$

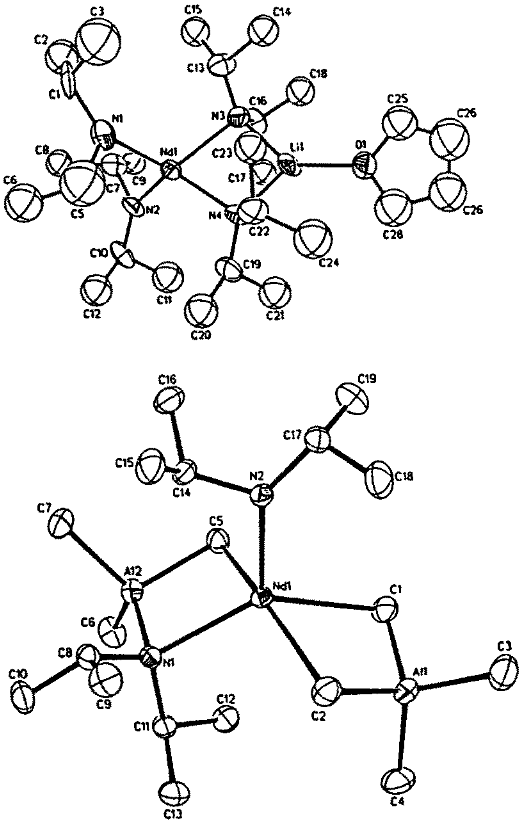


Fig. 7. ORTEP view of $Li(THF)Nd(N\textit{i}Pr_2)_4$ and $Nd(N\textit{i}Pr)_2(Me)(AlMe_3)_2$ [82]

group and a completely converted, "final" $[(\mu\text{-}Me)_2AlMe_2]$ unit. The formation of $Nd(N\textit{i}Pr)_2(Me)(AlMe_3)_2$ formally involves the stoichiometry shown in Eq. (9), although the actual route may be much more complicated.

$$Nd(N\textit{i}Pr_2)_3(THF) + 3AlMe_3 \rightarrow Nd(N\textit{i}Pr_2)_2(Me)(AlMe_3)_2 + [\textit{i}Pr_2NAlMe_2] \qquad (9)$$

The most interesting structural feature is the extremely short terminal Nd–N distance of 2.167(2) Å, which resembles Ln–O bond lengths [18]. This cannot be explained in terms of a "double bond". However, as a common feature in all aforementioned $Ln{-}N\textit{i}Pr_2$ complexes, close Ln···C interactions play a crucial part on steric saturation (Table 3). In $Nd(N\textit{i}Pr)_2(Me)(AlMe_3)_2$ a Ln···C contact of 2.934(2) Å could be observed. For comparison $M(N\textit{i}Pr_2)_3$ (M = Al, Cr) do not show close Ln···C contacts [85].

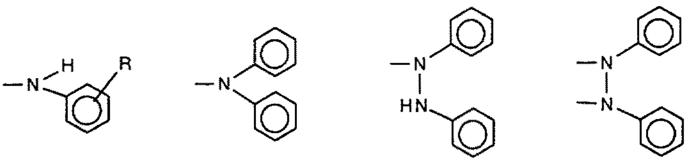
Alkylidene amide complexes of type $[(RCp)_2Y(N{=}CHR')]_2$ (R = H, Me; R′ = Me, *t*Bu) were generated via 1,2 addition of $[(RCp)_2YH(THF)]_2$ to the nitriles

Table 3. M–N(EHMe$_2$)$_2$ complexes with close M···E contacts (E = C, Si)

Compound	M···E [Å]	M–N–E "a" [°]	M–N–E "b" [°]	Ref.
LiNd(N*i*Pr)$_2$(μ-N*i*Pr$_2$)$_2$(THF)	2.95(2)	101.8(13)	139.5(4)	[82]
	3.00(2)	104.5(12)	140.9(13)	
	2.99(2)	98.9(12)	123.7(13)	
	2.98(2)	97.1(12)	127.5(13)	
LiLa(N*i*Pr$_2$)$_2$[μ-P(C$_6$H$_4$OMe-*o*)$_2$]$_2$(THF)	3.044	105.6(9)	141(1)	[79]
Nd(N*i*Pr$_2$)$_2$Me(AlMe$_3$)$_2$	2.934(2)	106.1(1)	138.3(2)	[83]
{ZrCl(μ-Cl)[N(SiHMe$_2$)$_2$]$_2$}$_2$	2.943(1)	102.8(2)	129.6(2)	[90]
Cp$_2$Zr(H)(N*t*BuSiHMe$_2$)	2.857(2)	95.1(2)	139.8(5)	[91]
	2.853(2)	92.6(3)	136.8(4)	
Cp$_2$Zr(Cl)(N*t*BuSiHMe$_2$)	2.931(1)	99.1(1)	137.3(2)	[91]

R'CN (Table 2) [86]. The molecular structure of the 2,2-dimethylpropanonitrile derivative contains unsymmetrically bridging alkylidene amide ligands. Reaction of the yttrium and erbium hydride species with isonitrile results in the formation of a formidoyl moiety (Table 2) [87]. Surprisingly the Ln–N interaction is in the range of the nitrile product. A similar molecular structure was found in the oximato complex [Cp$_2$Gd(μ-η^2-ONCMe$_2$)]$_2$ (Gd-N$_{av}$ 2.42(1) Å) [88].

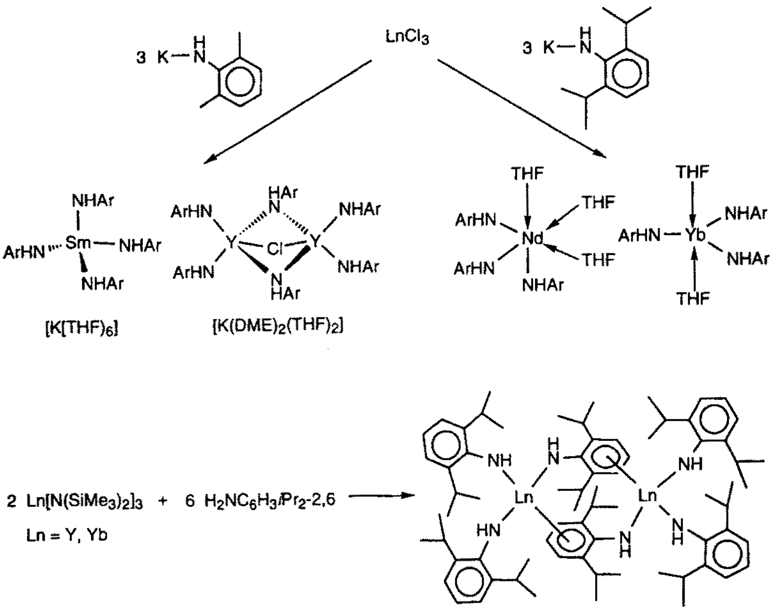
3.2 Aryl-Substituted Ligands



R = H, Me, 2,6-Me$_2$, 2,6-*i*Pr$_2$, 4-OMe

Unlike their O-counterparts, namely the aryloxides [92], the anilides have gained entry into lanthanide chemistry only very recently [93]. Their suitability as ligands in *f*-element chemistry was demonstrated in [K(THF)$_2$][U(NHC$_6$H$_3$*i*Pr$_2$-2,6)$_5$] [94].

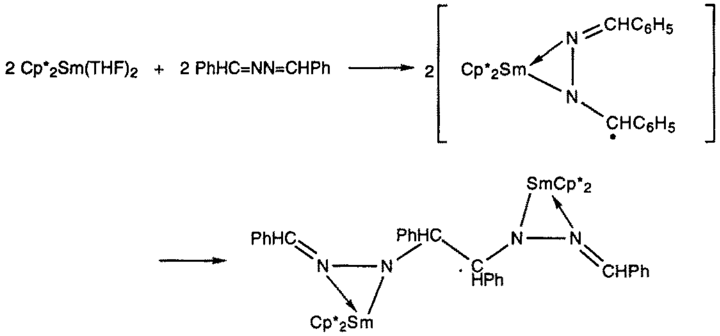
Corresponding aryloxide [95] and anilide complexes (Scheme 5) [93] show similar structural features as evidenced in Yb(NHC$_6$H$_3$ *i*Pr$_2$-2,6)$_3$ (THF)$_2$ and [Yb(NHC$_6$H$_3$*i*Pr$_2$-2,6)$_3$]$_2$. The latter, donor solvent free complex which was obtained according to the silylamide route (Sect. 7.1) shows Y-η^6-arene bridging (Y-arene(center) 2.34, 2.64 Å). Again, less bulky ligands such as 2,6-dimethylanilide tend to *ate* complexation. However, unlike in the above mentioned diisopropyl amide, separated ion pairs as in complex [K(THF)$_6$][Ln(NHC$_6$H$_3$Me$_2$-2,6)$_4$] (Ln = Nd, Sm) also resulted [93]. An unexpected, heteroligand bridged



Scheme 5. Effect of aryl substitution and method of preparation on anilide complexes

complex, $[K(THF)][Y_2(\mu\text{-}Cl)(\mu\text{-}NC_6H_3Me_2\text{-}2,6)(NC_6H_3Me_2\text{-}2,6)_4(THF)_2]$ was formed by employing one of the smaller lanthanide elements (Y–Cl 2.806(8), 2.807(8) Å). As expected, anilides are also accessible for adduct formation with group(IIIb) alkyls and subsequent alkylation reactions (Sect. 7.1).

The sterically more crowded diphenylamide derivatives have been mainly reported in form of heteroleptic complexes along with the cyclopentadienyl ligand (Table 4) [96, 97]. Related phenyl substituted hydrazine complexes have been used in Sm(II) mediated reactions (Table 4) [98]. Reaction of decamethylsamarocene with benzaldehyde azine resulted in a coupled product (Eq. 10) [99]. $SmCp_2^{*+}$ stabilized radical anions are assumed to be intermediates during the coupling process.



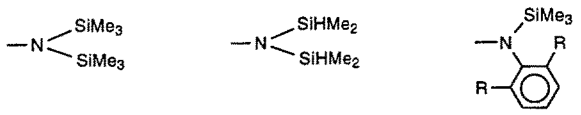
(10)

Table 4. Arylamide and hydrazide derived complexes

Compound	Ln–N [Å]	Ref.
$[K(THF)_6][Sm(NHC_6H_3Me_2\text{-}2,6)_4]$	2.340(8), 2.356(9), 2.367(9), 2.468(7)	[93]
$[K(THF)][Y_2(\mu\text{-}Cl)(\mu\text{-}NC_6H_3Me_2\text{-}2,6)(NC_6H_3Me_2\text{-}2,6)_4(THF)_2]$	2.268(2), 2.28(2), 2.29(2), 2.30(2), 2.39(2), 2.40(2), 2.54(2), 2.55(2)	[93]
$[Nd(NH\text{–}C_6H_3\text{–}i\text{Pr}_2\text{-}2,6)_3(THF)_3](THF)$	2.304(8), 2.304(8), 2.320(8)	[93]
$Yb(NH\text{–}C_6H_3\text{–}i\text{Pr}_2\text{-}2,6)_3(THF)_2$	2.14(1), 2.17(1), 2.20(2)	[93]
$\{(AlMe_4)_2Nd[(\mu_3\text{-}NC_6H_5)(\mu\text{-}Me)AlMe]\}_2$[a]	2.401(5)	[93]
$Cp^*_2Sm(NHPh)(THF)$	2.331(3)	[65b]
$[Li(DME)_3][Cp_2Nd(NPh_2)_2]$	2.421(7), 2.434(7)	[97a]
$[Li(THF)_4][Cp_2Lu(NPh_2)_2]$	2.290(7), 2.293(7)	[96]
$[Li(DME)_3][(MeCp)La(NPh_2)_3]$	av. 2.459(7)	[97b]
$[Li(THF)_4][(t\text{BuCp})Yb(NPh_2)_3]$	2.284(9), 2.234(1), 2.274(9)	[97c]
$[Cp^*(THF)Sm]_2[N_2Ph_2]_2$	2.323(8),	[98b]
$Cp^*_2Sm(N_2Ph_2)(THF)$	2.39(1), 2.42(1), 2.40(1), 2.45(1)	[98b]
$[Cp^*_2Sm]_2(\mu\text{-}\eta^1:\eta^1\text{-}N_2Ph_2)$	2.40(1), 2.41(1)	[98a]
$Cp^*_2Sm(\eta^2\text{-}PhNHNPh)(THF)$	2.330(5)	[65b]
$[Cp^*_2Sm]_2[\mu,\ \eta^4\text{-}(PhHC{=}NNCHPh\text{-})_2]$	2.31(1), 2.43(1)	[99]
$[Cp(THF)Yb]_2[N_2Ph_2]_2$	2.206(5), 2.188(5), 2.487(5), 2.572(5)	[98b]

[a] Sect. 7.1.

4 Silylamides



R = H, Me, *i*Pr

The most discussed ligand in lanthanide amide chemistry to date is probably the bis(trimethylsilyl) amide ligand, often abbreviated as btsa or $N(TMS)_2$. The pioneering work with this ligand was conducted by Bürger and Wannagat, who synthesized the useful alkali metal amides M(btsa) [100] and the first d-transition metal complexes [101]. Afterwards the steric bulk of the btsa ligand proved to be predetermined for generation of low coordination numbers at metal centers including the first 3-coordinated d-transition metal complexes [102]. The stabilization of low oxidation states of metals was also tackled [19]. Scheme 6 reflects the steric bulk of the btsa ligand in numbers compared with an arbitrary selection of some other common bulky ligands. These steric coordination numbers have been introduced for f-elements as a response to the dominating part of steric effects [103]. The synthetic value of the btsa complexes is discussed in Sect. 7.1.

O*t*Bu	Cp	$N(SiMe_3)_2$	$CH(SiMe_3)_2$	$OC_6H_3tBu_2$-2,6	Cp*	COT	OEP
1.40	2.04	2.17	2.24	2.41	2.49	3.44	4.30

Scheme 6. Selected steric coordination numbers according to [103]

4.1 Lanthanide(III) Complexes

4.1.1 Homoleptic Bis(trimethylsilyl)amide Complexes

The introduction of the btsa ligand into lanthanide chemistry by Bradley led to the isolation of the homoleptic compounds $Ln(btsa)_3$ [7], interpreted as the first 3-coordinate lanthanide complexes. This result was indeed spectacular and exploration of the chemical and physical properties of this "simple" system is continuing [104–106].

The original synthesis started from the dehydrated lanthanide halides and Li(btsa), prepared in situ from *n*BuLi and $HN(SiMe_3)_2$ in THF at room temperature, subsequent extraction with hexane and final sublimation at 75–100 °C/10^{-4} mbar [7c]. Meanwhile the demand for its ready availability led to more work on reaction conditions and appropriate starting reagents. A slight excess of freshly prepared lanthanide trihalides and the use of sodium or potassium btsa precursors seemed advantageous. Use of Li(btsa) results in product contaminations such as, e.g., $[Li(btsa)(THF)]_2$ [107]. In this way the $Ln(btsa)_3$ systems can be synthesized in high yield (> 90%) and obtained very pure and donor-solvent free via sublimation. Isolation by recrystallization without previous sublimation can lead to product contamination with *ate* complexes of type $Nd(btsa)_3(\mu\text{-}Cl)Li(THF)_3$ [84] and $[Y(btsa)_3(Cl)][Li(THF)_4]$ [108]. Another successful synthesis starts from the lanthanide triflates $Ln(O_3SCF_3)_3$ [109]. IR spectroscopy has proven to be an excellent tool for quick determination of the amide purity [22a,110]. Specific for each lanthanide metal is the $\nu_{as}(LnNSi_2)$ stretching mode, the energy of which decreases from La (1007 cm^{-1}) to Lu (974 cm^{-1}), the smallest lanthanide forming the strongest Ln–N bond. EI mass spectroscopic studies show the parent molecular ions and the strongest metal-containing ion by loss of one protonated ligand. Anomalies have been detected in the course of these investigations for those elements which are accessible for the divalent oxidation state [111].

However, the molecular structure of the $Ln(btsa)_3$ complexes was the most interesting feature. Herein the lanthanide metals adopt a pyramidal geometry, independent on the size of the metal as well the state of matter [22a, 108, 112–115]. In contrast, main and d-transition metals exhibit planar geometry [19c].

Figure 8 shows the molecular structure of the solid dysprosium analog. Because of the D_3 site symmetry (space group $P\bar{3}1c$) the molecule shows a disordering along the crystallographic z axis. This is expressed in a simplified disordering model. Bond distances and angles which go with it are summarized in Table 5.

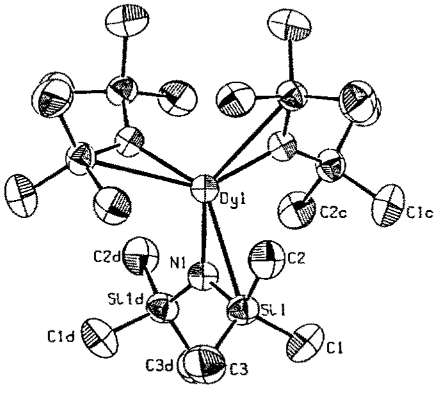
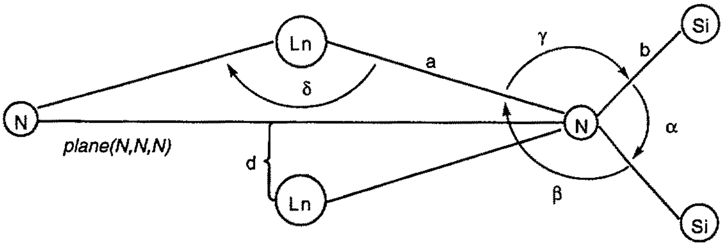


Fig. 8. Solid state structure of Dy(btsa)$_3$ [115]

Table 5. Structural data for Ln(btsa)$_3$



Ln	a [Å]	b [Å]	d [Å]	α [°]	β [°]	γ [°]	δ [°]	Ref.
solid								
Sc	2.047(6)	1.751(2)	0.44	121.6(4)	–	–	115.5	[112]
Nd	2.29(4)	1.70(1)	0.34	126.4(9)	123.2(5)	110.1(4)	117.8(1)	[113]
Eu	2.259(9)	1.702(3)	0.42	126.0(6)	–	–	116.6	[112]
Dy	2.212(2)	1.717(3)	0.52	123.6(4)	128.2(2)	107.5(2)	114.6(1)	[115]
Y	2.224(6)	1.716(3)	0.53	124.3(4)	127.8(2)	107.1(2)	114.63(4)	[108]
Er	2.21(1)		0.58	123.7(8)	129.2(4)	106.2(3)	113.4(2)	[115]
Yb	2.158(13)	1.72(4)	0.40	122.1(8)	–	–	–	[22a]
gas								
Sc	2.02(3)	1.715(8)	0.14	128(2)	116.0(1)	116.0(1)	119.5(15)	[114a]
La	–	–	–	–	–	–	110(3)	[114b]
Ce	2.33(4)	1.696(15)	0.67	129(4)	123(2)	108(2)	112(3)	[114b]
Pr	2.31(4)	1.705(15)	0.62	129(4)	123(2)	108(2)	113(3)	[114b]
Lu	2.168(12)	1.712(5)	0.51	130.6(5)	123.9(5)	105.5(4)	114.4(4)	[115b]

The trigonal pyramidal molecular structure has been subjected to numerous interpretations. In Sc(btsa)$_3$ the pyramidal ScN$_3$ fragment was ascribed to crystal packing because the nonplanarity is lost in the gas phase [114a]. Electric dipole moment measurements confirmed a planarity in dilute benzene solutions [106a]. Zero dipole moments are also obtained for the larger lanthanide metals

[22a]. Additionally, the characteristic doublet of the LnN_3 stretching vibration (at about 385 and 370 cm^{-1}), which is required for the pyramidal LnN_3 configuration, collapses into one band in solution [22a]. However, in case of the lanthanide metals the LnN_3 configuration is pyramidal again in the gas phase and that should exclude crystal packing effects [114b].

The lack of "dative bonds" has been used as an argument for the pyramidal LnN_3 geometry. Lanthanide elements are not able to form $N \rightarrow Ln$ π-interactions with the btsa ligand due to the limited extension of their f-orbitals. However, the existence of dative bonds in planar, homoleptic group(IIIB) metal (pπ-pπ) and 3d metal (dπ-pπ) btsa complexes could not be confirmed either [82]. Lone-pair interactions and M–N π bonding also seemed to be unlikely from photoelectron studies [116] and by the observed large torsion angles of the NSi_2 moiety.

The attribution of stereochemically active non-bonding electrons to yield non-planarity could also be excluded because of the pyramidal GED structure of $La(btsa)_3$ (f^0). Fjeldberg and Andersen suggested two factors which determine the observed geometries [114]. First, nonbonding interligand (C···C) repulsions favor the planar form. Second, the pyramidal configuration is stabilized through charge induced dipole interactions [117]. The latter interpretation is also relevant for unusual bent structures like $SmCp_2^*$ [118]. However, both arguments might be rejected in the $Ln(btsa)_3$ case. The nonbonding interligand (C···C) repulsions are significantly even longer in the pyramidal solid form of the scandium derivative compared to its planar GED structure. The effect of polarization and consequently a transition to planarity is not visible in the gas-phase structure of $Lu(btsa)_3$, which contains the smallest and less polarizable lanthanide cation.

Another interpretation which the author favors is based on short Ln···Si contacts [119]. These distances lie clearly within the sum of van der Waals radii of Ln and Si, e.g., 3.18 Å for Dy···Si [115], and should allow the stabilization of nonplanar LnN_3 moieties. Consequently, those additional Ln···Si contacts change the coordination number of the metal center from 3 to 6 as indicated in Fig. 8. A remarkable discrepancy in the Ln–N–Si angle is observed. The close contacts can stabilize the LnN_3 fragment in the solid and gas phase where no other coordination site is present. However, in solution, especially benzene or toluene, Ln···solvent contacts compete with the weak Ln···Si contacts and thus might explain the planarity of the LnN_3 fragment in solution.

Finally, the origin of those interactions awaits an answer. They are often called agostic interactions, and usually appear with metal centers in low formal coordination numbers. The perturbation of the $SiMe_3$ group is even more distinct in complexes with the $CH(SiMe_3)_2$ moiety [120], where longer Ln–C σ-bonds allow a better "agostic approach". In recent theoretical [121] and NMR studies [122], the phenomenon has been attributed to interactions between the electron-deficient lanthanide cation and the electron density of the Si-C bond. Certainly the expanded size of the lanthanide cations may support these interactions but cannot be given as the only reason. For example, the thallium

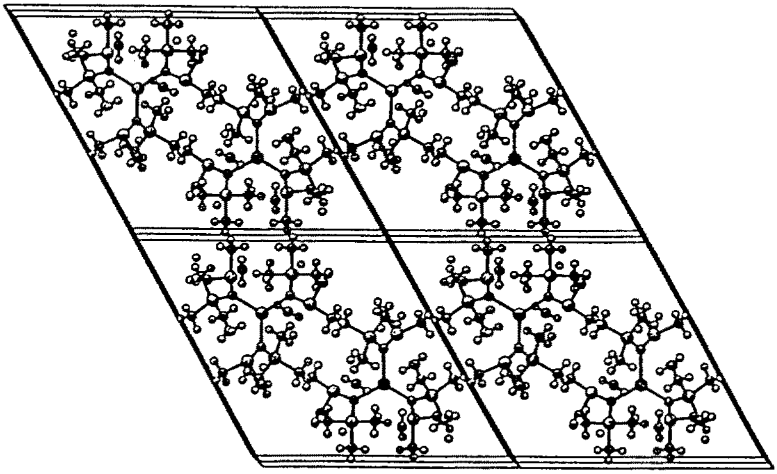


Fig. 9. View of the z axis along with the unit cell of Dy(btsa)$_3$ [115]

derivative is planar in the solid state [123], whereas the complex with the smaller scandium is pyramidal. Thus the structural feature might be best ascribed to a synergism of cation size, enhanced Lewis acidity of the metal center and the ionic character of the Ln–N bond.

Another interesting feature of the solid state structure is the long range packing of the Ln(btsa)$_3$ molecules (Fig. 9). The presence of large hexagonal spaces within the crystal lattice might induce a facile phase transition, e.g., reorientation of the molecules in the crystalline lattice [115] and inclusion of solvent molecules [99b,108], and therefore be responsible for the lack of quality of the solid state structure determinations.

4.1.2 Mixed Ligand (Heteroleptic) Complexes

A considerable number of adduct and heteroleptic silylamide complexes has been reported (Table 6) [124–137]. In the following they are summarized with respect to their ligand combination.

Adducts Ln(btsa)$_3$(A). The availability of additional coordination sites was shown in Ln(btsa)$_3$ complexes by isolation of their mono adducts OC(PPh$_3$) [124] and OCPh$_2$ [125], respectively, and their bis adducts of benzonitril [108]. The stabilizing Ln···Si contacts in the homoleptic Ln(btsa)$_3$ systems are obviously replaced by a stronger hard Ln ← donor atom coordination. Other adduct complexes include the donating molecules THF [84], NC*t*Bu and CN*t*Bu [109b].

Ln(btsa)$_2$(Cl). The mixed amide/halide derivatives are of synthetic value because the Ln–Cl bonds (Gd: 2.740(4) Å, 2.765(4); Yb: 2.667(4), 2.690(4)) are available for

Table 6. Ln–N-bond lengths in heteroleptic Ln(III) silylamide complexes

Compound	d(Ln-N(btsa)) [Å]	Ref.
adducts		
La[N(SiMe$_3$)$_2$]$_3$(PPh$_3$O)	2.41(2)	[124a]
Tb[N(SiMe$_3$)$_2$]$_3$(Ph$_2$CO)	2.26(1), 2.26(1), 2.28(1)	[125]
Y[N(SiMe$_3$)$_2$]$_3$(NCPh)$_2$	2.248(4), 2.257(4), 2.265(4)	[108]
heteroleptic complexes		
{Gd[N(SiMe$_3$)$_2$]$_2$(μ-Cl)(THF)}$_2$	2.239(5), 2.264(5)	[126]
{Yb[N(SiMe$_3$)$_2$]$_2$(μ-Cl)(THF)}$_2$	2.174(5), 2.198(5)	[126]
Nd[N(SiMe$_3$)$_2$]$_3$(μ-Cl)Li(THF)$_3$	2.324(8), 2.335(8), 2.348(8)	[84]
{Y[N(SiMe$_3$)$_2$]$_3$(Cl)}[Li(THF)$_4$]	av. 2.25	[108]
La$_2$[N(SiMe$_3$)$_2$]$_4$(O$_2$)(PPh$_3$O)	2.37(2), 2.49(2)	[124a]
Yb[N(SiMe$_3$)$_2$][OC*t*Bu(2-CH$_2$–NC$_5$H$_3$–Me-6)$_2$]$_2$	2.260(5)	[127]
Y[N(SiMe$_3$)$_2$]$_2$[OSi*t*Bu(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$]	2.221(9), 2.237(9)	[128]
{Nd[N(SiMe$_3$)$_2$]$_3$(OSiMe$_3$)}Li(THF)$_4$	2.36(1), 2.38(1), 2.40(1)	[84]
{Gd[N(SiMe$_3$)$_2$]$_2$(μ-S*t*Bu)}$_2$	2.230(6), 2.244(6)	[129]
La[N(SiMe$_3$)$_2$]$_2$(PPh$_2$)(PPh$_3$O)$_2$	2.40(1)	[130b]
{Cp*CeI[N(SiMe$_3$)$_2$]}$_2$	2.308(4)	[132]
Cp*Ce[N(SiMe$_3$)$_2$]$_2$	2.357(7), 2.349(7)	[132]
Cp$^*_2$YN(SiMe$_3$)$_2$	2.274(5), 2.253(5)	[133]
Cp$^*_2$SmN(SiMe$_3$)$_2$	2.301(3)	[134]
(*S*)-Me$_2$Si(Me$_4$C$_5$)[(+)-neomenthyl-Cp]SmN(SiMe$_3$)$_2$	2.300(5)	[135]
(*S*)-Me$_2$Si(Me$_4$C$_5$)[(−)-menthyl-Cp]SmN(SiMe$_3$)$_2$	2.302(9)	[135]
(*R*)-Me$_2$Si(Me$_4$C$_5$)[(−)-menthyl-Cp]YN(SiMe$_3$)$_2$	2.211(8), 2.281(8)	[135]
(COT)Lu[N(SiMe$_3$)$_2$](THF)	2.197(3)	[136]
{[N(SiMe$_3$)$_2$]$_2$Sm}$_2$[μ-(η^8:η^8-COT)]	2.275(2), 2.286(2)	[136]
Y[N(SiMe$_3$)$_2$](DAC)[a]	2.338(11)	[137]

[a] See Sect. 5.1.

simple metathesis reactions. The dimeric compounds are assumed to be less stable for metals larger than europium due to steric unsaturation. Already the europium derivative disproportionates in solution to Eu(btsa)$_3$ and EuCl$_3$ [126].

Ln(btsa)(OR)$_2$. Very recently the first mixed amide/alkoxide complexes of lanthanide(III) have been obtained (Fig. 10) [127, 128]. Bulky, donorfunctionalized alkoxide ligands seem to allow the formation of such unusual heteroleptic complexes in varying ligand combinations via the silylamide route. In particular, amide displacement by alcohols is not readily controllable and exclusive exchange is usually observed. In Yb[OC*t*Bu(2-CH$_2$–NC$_5$H$_3$–Me-6)$_2$]$_2$(btsa) two O–N-bidentate alkoxide ligands (Ln–O$_{av}$ 2.065(4) Å) occupy the basal sites of a distorted square pyramidal coordination polyhedron. The axial Yb–N(btsa) bond is comparatively elongated.

Ln(btsa)$_2$*(SR)*. Complex [Gd(btsa)$_2$(μ-S*t*Bu)]$_2$ has been the first structurally characterized lanthanide thiolate complex (Gd–S, 2.760(5), 2.823(5) Å) and was

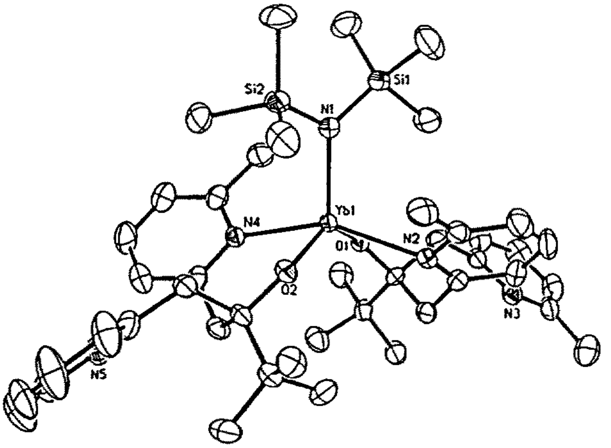


Fig. 10. Molecular structure of Yb[OC*t*Bu(2-CH_2-NC_5H_3Me-6$)_2$]$_2$(btsa) [127]

prepared by simple metathesis reaction from the aforementioned chloride precursors [129].

Ln(btsa)$_2$*(PR*$_2$*)*. The diphenylphosphido complex La(btsa)$_2$(PPh_2)($OPPh_3$)$_2$ (La–P, 3.165(6) Å) was prepared according to the silylamide route [130b].

Ln(btsa)$_x$*(Cp)*$_y$*(*$x = 1, 2$; $x + y = 3$*)*. Monomeric complexes of this type have been generated in different ratios [131–135]. The mono cyclopentadienyl derivatives have been prepared according to the advantageous aryloxide route [132]. A common feature in all those formally unsaturated complexes is the stabilization through close intramolecular Ln···C($SiMe_3$) contacts in the range 2.9–3.1 Å [132]. Chiral C1-symmetric organolanthanide amides of type $Me_2SiCpMe_4$(R*Cp)Ln(btsa) can be prepared as diasteromerically pure crystalline compounds [135]. During the amidation reaction of the chiral chloride precursors $Me_2SiCpMe_4$(R*Cp)Ln(μ-Cl)$_2$Li(OEt_2)$_2$ epimerization can occur. The degree of epimerization is strongly dependent on the reaction conditions, identity of R*, the initial configuration of the chloro complex, the Ln ionic radius and the alkali ion in M(btsa). When isolated, the amide complexes are configurationally stable even after 48 h at 60 °C in toluene. Protonolysis by, e.g., alkylamines results in facile epimerization. Their application in catalytic hydroamination/cyclization reactions is discussed in Sect. 7.3.

Ln(btsa)(COT). Reaction of [(COT)Sm(μ-Cl)(THF)]$_2$ with Na(btsa) did not yield the simple metathesis product (COT)Ln(btsa)(THF) as in the Y-, Gd-, Er- and Lu-case [136]. Amazingly, an inverse sandwich complex was obtained in the form of [(btsa)$_2$Sm]$_2$[μ-(η^8:η^8-COT)] with elongated Sm-C(COT) bond lengths (av 2.688(5) Å) and close Sm···C(btsa) contacts (2.970(2), 3.105(2) Å) (Fig. 11).

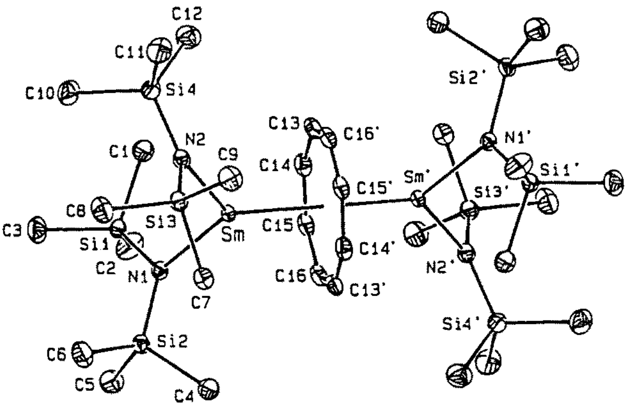


Fig. 11. Molecular structure of $[(btsa)_2Sm]_2[\mu\text{-}(\eta^8{:}\eta^8\text{-COT})]$ [136]

4.1.3 Bis(dimethylsilyl)amide Complexes

Limited application of the original silylamide route (Sect. 7.1) led to the exploration of the sterically less crowded bis(dimethylsilyl)amide (bdsa) ligand which is also readily available [138]. In contrast to the very similar $NiPr_2$ ligand, the bdsa ligand enables the isolation of pure products via the stoichiometric $LnCl_3$/Li(bdsa) procedure and this favors this system as a synthetic precursor.

A distorted trigonal bipyramidal geometry is representative for $Ln(bdsa)_3(THF)_2$ in the solid state, with the THF molecules occupying the apical positions (Fig. 12) [115]. They represent the first complexes with three bdsa ligands attached to a metal center. Two other metal bdsa systems have been structurally characterized, $\{MMe_2[\mu\text{-}N(SiHMe_2)]\}_2$ (M = Al, Ga) [139] and $\{Zr[N(SiHMe_2)_2]_2Cl(\mu\text{-}Cl)\}_2$ [90]. Despite the fact that there is an unusual long-wave shifted ν(Si-H)-vibration which is indicative of agostic interactions [90], the molecules show neither close Ln···Si contacts nor anomalies in the Ln–N–Si angles in the solid state, probably due to the presence of coordinating THF at the Ln center. Close Ln···E contacts were discussed in previous sections for solvent free $Ln(btsa)_3$ and $Ln(NiPr_2)_3$ complexes and are also known for the $N(SiHMe_2)_2$ fragment, e.g., in unsolvated $\{Zr[N(SiHMe_2)_2]_2Cl(\mu\text{-}Cl)\}_2$ [90].

CI mass spectroscopic studies at temperatures < 100 °C show the parent molecular ions, but sublimation does not proceed as smoothly as with solvent free $Ln(btsa)_3$. Application of higher temperatures (ca. 150 °C) results in the release of THF followed by the detection of dinuclear species in the mass spectra. The THF ligands in $Y(bdsa)_3(THF)_2$ could be replaced by stronger donor molecules as the carbene ligand 1,4-dimethylimidazol-2-ylidene [140]. The bdsa ligand is rather flexible in these exchange reactions to afford both mono, Y(bdsa)(L), and bis(carbene) adducts $Y(bdsa)(L_2)$, respectively.

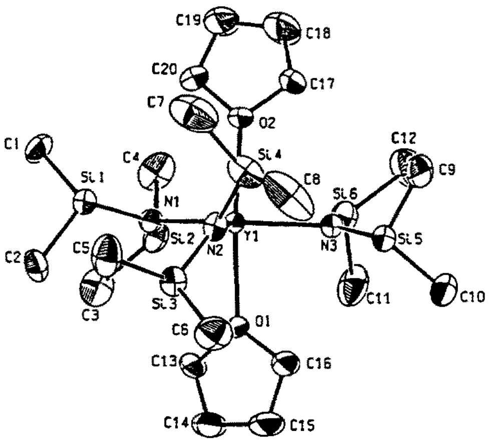


Fig. 12. ORTEP view of $Y(bdsa)_3(THF)_2$ (Y–N 2.275 Å, 2.229(4), 2.276(4); Nd-N 2.253(4), 2.326(5), 2.351(5)) [115]

4.1.4 Phenyltrimethylsilylamide Complexes

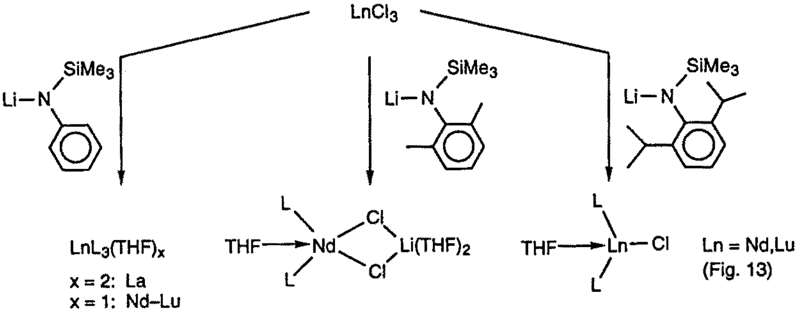
Steric fine-tuning in silylamide complexes could also be achieved by introducing N(phenyl)-substituted silylamides (Scheme 7) [141]. As observed in the anilide complexes [93], variation of the steric bulk in 2,6-position of the phenyl ring causes different structural chemistry. The phenyl-substituted silylamides are not sublimable.

In complexes bearing phenyl-unsubstituted ligands, $Ln[N(Ph)(SiMe_3)]_3(THF)_x$, accommodation of two additional THF ligands comparable to $Ln(bdsa)_3(THF)_2$ is detected only in the presence of the largest lanthanide element, lanthanum. In corresponding complexes of the smaller lanthanide elements close Ln···C contacts with the quaternary (2.846(3)–3.069(3) Å) and ortho phenyl carbon atoms (3.027(3)–3.378(4) Å) saturate the metal center. These interactions are further documented in the difference between the Nd-N-Si (128.9(1)–138.7(1)°) and Nd-N-Cα angles (99.9(2)–122.2(2)°).

In the 2,6-dimethylphenyl-case, the formation of an LiCl *ate* -complex is favored, rendering the metal center in a distorted trigonal bipyramidal geometry. The steric hindrance of 2,6-diisopropyl-substitution allows the isolation of an interesting formally 4-coordinate complex with a terminal Ln–Cl bond (Fig. 13; Nd-Cl 2.617(1) Å). Again, both heteroleptic complexes exhibit close Ln···Cα interactions in the range of 2.814(2)–3.129(2) Å.

4.2 Lanthanide(II) Complexes

Basic work in this field has been done by Andersen with the elements ytterbium and europium [142–145]. More recently complexes with the stronger reducing



Scheme 7. Effect of aryl substitution on phenyltrimethylsilylamide complexes

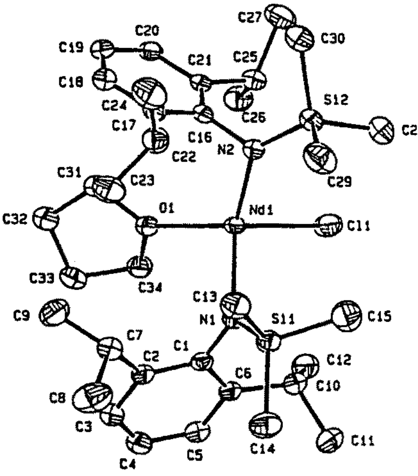


Fig. 13. Molecular structure of $NdCl[N(C_6H_3iPr_2\text{-}2,6)(SiMe_3)]_2(THF)$ [141]

samarium(II) have been examined [89, 146]. As for the trivalent systems, both homoleptic and heteroleptic complexes were synthesized (Tables 8 and 9).

4.2.1 Homoleptic Complexes

$[Yb(btsa)_2]_2$ was prepared according to the toluene method from the adduct complex $Yb(btsa)_2(OEt_2)_2$ [145, 147]. The dimeric constitution was proven by X-ray analysis and revealed to be isostructural to the calcium derivative [148] (Fig. 14). The ytterbium atoms form close $Yb\cdots C(SiMe_3)$ contacts with both one bridging (2.820(4), 2.823(4) Å) and two terminal (2.785(4), 2.823(4) Å) btsa ligands to achieve steric saturation through 5-coordination. The samarium analogue could not be prepared according to this procedure because of its thermal lability undergoing disproportionation reactions including the formation of $Sm(btsa)_3$ [89].

Table 7. Ln–N-bond lengths in Ln(III) phenyltrimethylsilylamide complexes

Compound	d(Ln-N) [Å]	Ref.
$Nd[N(Ph)(SiMe_3)]_3(THF)$	2.298(2), 2.308(3), 2.320(3)	[141]
$Nd[N(C_6H_3Me_2\text{-}2,6)(SiMe_3)]_2(\mu\text{-}Cl)_2Li(THF)_2$	2.282(3), 2.318(3)	[141]
$NdCl[N(C_6H_3\mathit{i}Pr_2\text{-}2,6)(SiMe_3)]_2(THF)$	2.264(2), 2.276(2)	[141]

Table 8. Bond lengths in homoleptic Ln(II) silylamide complexes

Complex	d(Ln-N) [Å]	Ref.
$\{Yb[N(SiMe_3)_2]\}_2$	2.300(3), 2.310(3), 2.445(3), 2.492(3), 2.497(3), 2.573(3)	[147]
$\{NaEu[N(SiMe_3)_2]_3\}_n$	2.448(4), 2.554(4), 2.539(4)	[144]
$\{NaYb[N(SiMe_3)_2]_3\}_n$	2.38(2), 2.45(2), 2.47(2)	[144]
$\{NaSm[N(SiMe_3)_2]_3\}_n$	2.449(7), 2.554(6), 2.567(6)	[89]
$\{KSm[N(SiMe_3)_2]_3\}_n$	2.458(4), 2.529(3)	[89]

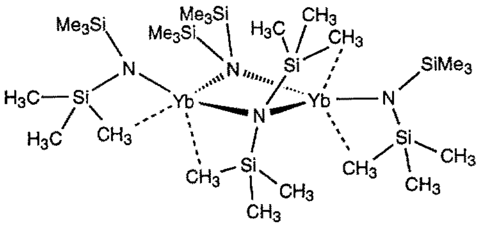


Fig. 14. Molecular drawing of $[Yb(btsa)_2]_2$ indicating the close Yb–C($SiMe_3$) contacts

Ate complexes

Several alkali metal (M) derived *ate* complexes have been prepared (Table 8). Again, the formation of such ternary systems is preferred. Even Sm(II) derivatives were readily available [89]. A common feature of the observed molecular structures are close inter- and intramolecular M···C as well as close Ln···Si van der Waals contacts which ensure steric saturation of the metal centers. Depending on the size of the alkali metal, different types of solid state structures are generated (Fig. 15). A comparison to the ammonia derived species in Sect. 2.1 can be drawn.

In $NaLn(btsa)_3$ (Ln = Sm, Eu, Yb) the sodium forms one close intermolecular Na···C($SiMe_3$) contact to build up chains of $NaLn(btsa)_3$ moieties. However, the larger potassium in $KSm(btsa)_3$ is linked by two intermolecular K···C($SiMe_3$) contacts to generate a 2-dimensional network. From the molecular structure (Fig. 15) it can be seen that all electropositive metals are encapsulated into the bulky ligand sphere caused by the intramolecular M···C

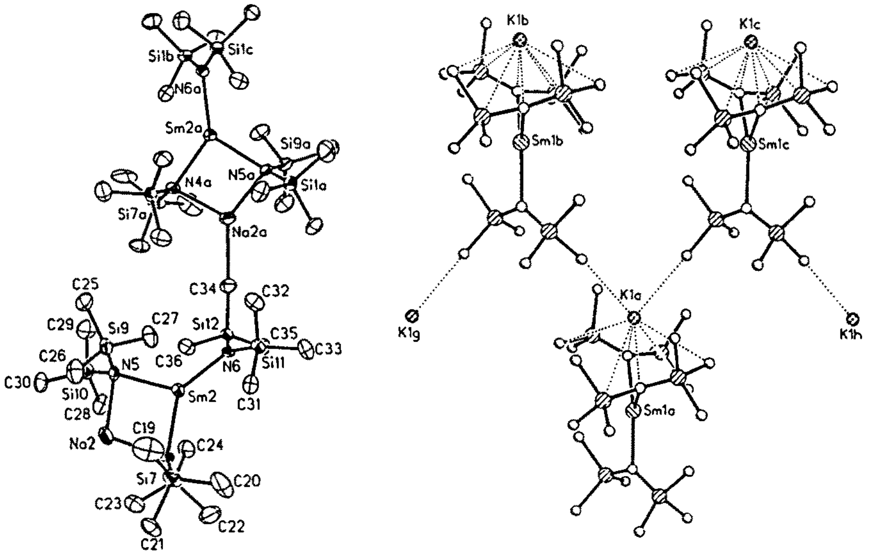


Fig. 15. Molecular structures of NaSm(btsa)$_3$ (*left*) and KSm(btsa)$_3$ (*right*) [89]

contacts. The shielding of the metals and the readily disrupted intermolecular contacts explain the good solubility even in nonpolar hydrocarbons. Facile deoligomerization and the stabilizing *ate* effect are also expressed in that MSm(btsa)$_3$ are sublimable at $< 100\,^{\circ}C$ under high vacuum. The *ate* complexes are potential mixed metallic precursors according the silylamide route.

4.2.2 Heteroleptic Complexes

Lanthanide(II) silylamide complexes which are obtained following the usual work up procedures are solvent adducts of, e.g., THF, Et_2O, DME, etc. These complexes are well characterized, soluble standard synthetic precursors (Table 9) [142,143,146]. Group(IIIB) metal alkyls are able to replace the co-ordinated solvent molecules to form mixed metallic complexes of type Ln(btsa)$_2$(MMe$_3$)$_2$ (M = Al, Ga; Table 9). Interaction of a lone electron pair on nitrogen with the strong Lewis acid is essential for the reaction. MMe$_3$ also displaces K(btsa) in the *ate* complexes described above to generate these heterobimetallic species. The molecular stucture of Sm(btsa)$_2$(GaMe$_3$)$_2$ is shown in (Fig. 16). The N–Sm–N angle of 131.7 °C resembles that in SmCp$^*_2$(THF)$_2$ (136.7°). Close Sm···C(SiMe$_3$) (3.051(3) Å) and Sm···C(GaMe$_3$) (av 2.902(3) Å) contacts result in a formal 8-coordination. Replacement of GaMe$_3$ by the stronger Lewis acid AlMe$_3$ to form Sm(btsa)$_2$(AlMe$_3$)$_2$ is straightforward.

A few "classic" heteroleptic complexes were sythesized involving additional lanthanide iodide [146], cyclopentadienyl [147, 149], amide [141], alkoxide

Table 9. Bond lengths in heteroleptic Ln(II) silylamide complexes

Complex	d(Ln-N(btsa)) [Å]	Ref.
$Sm[N(SiMe_3)_2]_2(THF)_2$[a]	2.442(9), 2.424(9)	[146]
$Eu[N(SiMe_3)_2]_2(DME)_2$	2.530(4)	[143]
$Yb[N(SiMe_3)_2]_2(DMPE)$	2.331(13)	[142]
$Sm[N(SiMe_3)_2]_2(GaMe_3)_2$[b]	2.510(2), 2.573(2)	[89]
$Yb[N(SiMe_3)_2]_2(AlMe_3)_2$	2.510(2), 2.573(2)	[145]
$\{Sm[N(SiMe_3)_2](\mu\text{-}I)(DME)(THF)\}_2$	2.455(7)	[146]
$\{KSmCp^*_2[N(SiMe_3)_2](THF)_2\}_n$	2.53(2)	[149]
$\{YbCp^*[\mu\text{-}N(SiMe_3)_2]\}_2$	2.445(3), 2.630(3)	[147]
$\{Yb[N(SiMe_3)_2](\mu\text{-tritox})\}_2$	2.332(6), 2.327(6)	[150]
$\{Yb[N(SiMe_3)_2]_2(\mu\text{-DAC})\}_2Yb$[c]	2.43(3), 2.44(3)	[140]
$Yb(Tp\text{-}t\text{Bu,Me})[N(SiMe_3)_2]$[d]	2.382(5)	[151]

[a] The Eu analogue is isostructural [89]

[b] The Sm–Al analogue is isostructural [89]

[c] See Sect. 5.1

[d] See Sect. 5.3

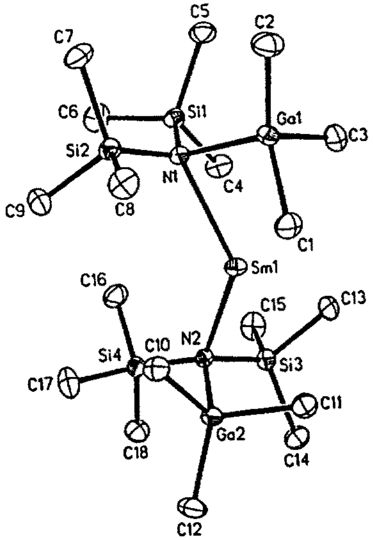
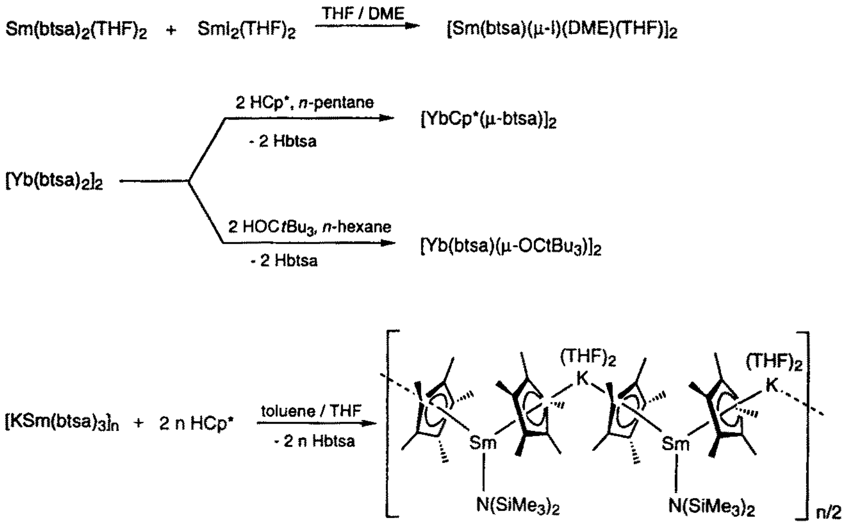


Fig. 16. ORTEP view of $Sm(btsa)_2(GaMe_3)_2$ [89]

[150] and pyrazolylborate ligands [151] (Scheme 8; Table 9). Complexes $[Ln(btsa)(X)]_2$ clearly show the grading of the bridging tendency of the varying ligands.

4.3 Cerium(IV) Complexes

While the investigation of Ce(IV) organyl [152] and alkoxide compounds [153] has attracted some attention, Ce(IV) amide chemistry was investigated in detail



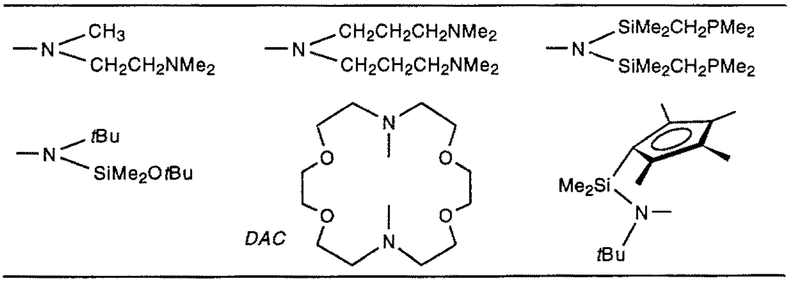
Scheme 8. Synthesis of heteroleptic lanthanide(II) silylamides

only for porphyrin and phthalocyanine systems (Sect. 6.3.2). These polycyclic systems have proven the stabilization of Ce(IV) by sole nitrogen environment and very recently the first synthesis and structural characterization of an organometallic amide, $Ce(btsa)_2(OtBu)_2$, was reported [154].

5 Complexes with Donorfunctionalized Ligands

Doubly charged chelating bisamide ligands of type $-NR-(CH_2)_nNR-$ have been known for a long time in main group and d-transition metal chemistry [19c]. Very recently tetradentate trisamide ligands have attracted attention, e.g., in form of azatitanatranes [155]. The simplest member of this family, $N(CH_2CH_2NH_2)_3$, already proved to be a suitable chelating ligand as shown in its neutral form [156]. Trimethylsilyl-substituted tripodal ligands provide an auxiliary coordination sphere in monomeric actinide complexes [157]. In lanthanide chemistry, investigation of complexes containing this type of multiple charged ligands has just started [158]. However, simply donorfunctionalized ligands (Table 10) have been applied successfully along with more sophisticated systems (Table 11). Multiply chelating amide ligands, derived from unsaturated macrocyclic systems, are treated separately in Sect. 6.3. A condensed section is devoted to polypyrazolylborato complexes. Complexes derived from chelating ligands such as benzamidinates [159], diiminophosphonates [160] and azaallyls [161] are reviewed by Edelmann [159].

5.1 Ligands Derived from Simple Amines and Silylamines



Again, *ate* complexation played an important part in the isolation of the donorfunctionalized complex $Li[Ho\{N(CH_3)CH_2CH_2N(CH_3)_2\}_4]$ with *N*,*N*,*N'*-trimethylethylendiamine as a bidentate ligand [162]. The expected homoleptic type LnL_3 could not be obtained by the 3:1 reaction. Another example involves the reaction of lithiated, commercially available $HN(CH_2CH_2CH_2NMe_2)_2$ with $SmCl_3$ to yield the heteroleptic *ate* complex $LiSm(\mu\text{-}L)L(\mu\text{-}Cl)Cl$ which contains both bridging and terminal Cl and amide ligands (Fig. 17) [163].

Linked cyclopentadienyl amide ligands have been introduced for scandium as a "next generation" ligand set in highly active single-component α-olefin polymerization catalysts [164]. In comparison to the more traditional bis(cyclopentadienyl) linked derivatives they should render the metal more Lewis acidic and more electron deficient. Additionally it was found that the bite angles, e.g., 102.5° in $[\{Cp^*SiMe_2(NtBu)\}Sc]_2(\mu\text{-}C_3H_7)_2$ are considerably less than for

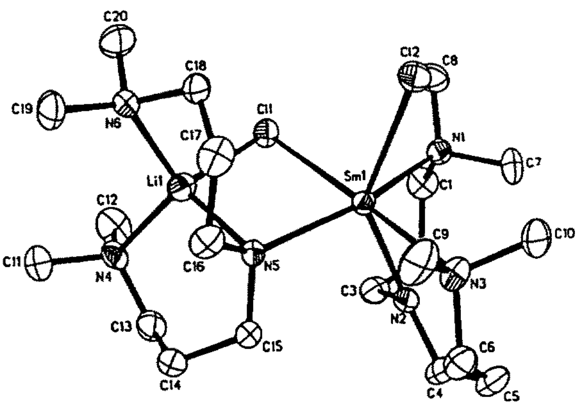


Fig. 17. ORTEP view of $LiSm[\mu\text{-}N(CH_2CH_2CH_2NMe_2)_2](\mu\text{-}Cl)[N(CH_2CH_2CH_2NMe_2)_2]Cl$ [163]

$Cp^*SiMe_2Cp^*$-type complexes which are typically in the range of 130–145°.

Deprotonated azacrowns of type DAC (4,13-diaza-18-crown-6) have been tested as new ancillary ligands [140]. They act like bisamide ligands with additional intramolecular O-donor functionalities and resemble, from the steric view, template ligands as COT or porphyrins. In the course of transamination reactions involving the oxidation states II and III, mixed amide lanthanide complexes were obtained. In monomeric Ln(DAC)(btsa) complexes, the three amide nitrogen atoms are arranged in a trigonal planar fashion around the metal center. The four ether oxygen atoms are located above and below the YN_3 plane. A similar geometry is found in the monomeric alkyl complex $Y(DAC)(CH_2SiMe_3)$ (Eq. 11c). Depending on the stoichiometry the reaction of divalent complex $Yb(btsa)_2(THF)_2$ yielded two products (Eq. 11a, b). The analogous Sm(II)-reaction resulted in oxidation to Sm(III) and isolation of Sm(DAC)(btsa).

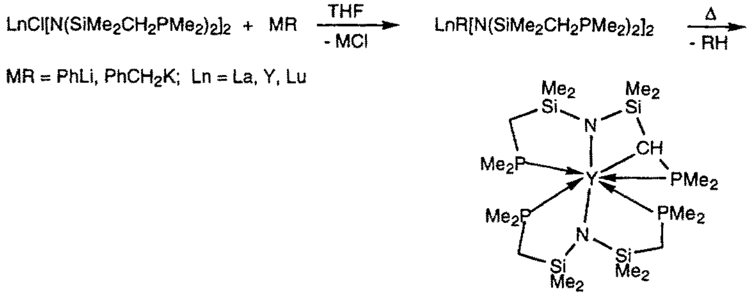
$$Yb[N(SiMe_3)_2]_2(OEt_2)_2 + H_2DAC \xrightarrow[-Hbtsa]{} \{Yb[N(SiMe_3)_2]_2(\mu\text{-}DAC)\}_2Yb \qquad (11a)$$

$$Yb{:}\ H_2DAC < 1.5{:}1$$

$$2Yb[N(SiMe_3)_2]_2(OEt_2)_2 + H_2DAC \longrightarrow \{Yb[N(SiMe_3)_2]_2\}_2(\mu\text{-}DAC) + 2Hbtsa \qquad (11b)$$

$$Y(CH_2SiMe_3)_3(THF)_2 + H_2DAC \longrightarrow Y(DAC)(CH_2SiMe_3) + 2SiMe_4 \qquad (11c)$$

The recent boom in modifying common ligands like cyclopentadienyls [165] or alkoxides [18] with donorfunctionalities to generate monomeric, more tractable complexes has also stimulated lanthanide silylamide chemistry. Two donorfunctionalized ligands have been reported. The phosphino substituted ligand $N(SiMe_2CH_2PR_2)_2$ (R = Me, *i*Pr, Ph) was introduced by Fryzuk to generate hard (metal)/soft (donor) contacts via hybrid chelation [166–169]. Two of these ligands can be anchored in a tridentate fashion to form four 5-membered metallacycles [167]. The particular ligand design allows the use of phosphorus NMR spectroscopy as a tool to assign the stereochemistry in these complexes [166]. The remaining chloride ligand was further derivatized with alkaline earth metal alkyls (Eq. 12). Hydrocarbyls thus formed are thermally labile and undergo hydrocarbon elimination via abstraction of a methylene proton (Eq. 12). This cyclometallation reaction [170] occurs for the larger lanthanum cation during the Cl/alkyl transformation. The observed Y–C bond length of 2.65(1) Å in $Y[N(SiMe_2CHPMe_2)(SiMe_2CH_2PMe_2)][N(SiMe_2CH_2PMe_2)_2]$ is elongated at about 0.2 Å in comparison to typical bond lengths, possibly due to the strain of the fused 3- and 4-membered rings.



(12)

Interestingly, the reaction of the chloride precursor with Grignard and diallyl magnesium reagents results in the formation of $\{Y[N(SiMe_2CH_2PMe_2)_2](\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2$ (Fig. 18, Table 10) [169]. Instead of the expected metathesis of chloride, one of the tridentate ligands was displaced. Normal metathesis was observed in the reaction of $Y[N(SiMe_2CH_2PMe_2)_2]Cl_2$ with $Mg(C_3H_5)_2$(dioxane). Monomeric derivatives of lanthanide(II) are also accessible to this ligand.

*t*Butoxysilylamide ligands were also tested as steric equivalents to the cyclopentadienyl ligand [171]. The divalent ytterbium complex $YbL_2(THF)_2$ could be isolated. However, Sm(II) is oxidized in analogous reactions. The homoleptic lanthanide(III) complexes are obtained only for the larger metals as in the case of neodymium (Table 10). Only two of those chelating ligands can be attached at the smaller ytterbium and like in cyclopentadienyl chemistry incorporation of alkaline halide is observed.

Ate complexation in aforementioned systems has been adventitious. The application of custom-made donorfunctionalized ligands should allow the intentional formation of heterobimetallic complexes of desired composition as it has already been shown in alkoxide chemistry [18].

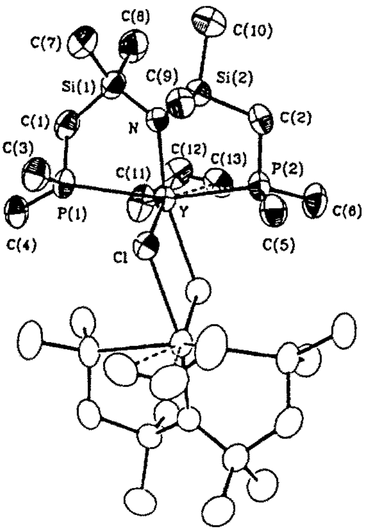


Fig. 18. ORTEP view of $\{Y[N(SiMe_2CH_2PMe_2)_2](\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)\}_2$ [169]

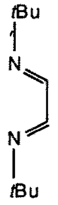
Table 10. Structurally characterized complexes with functionalized amide ligands

Compound	Ln–N	Ref.
$Li[Ho(NMeCH_2CH_2NMe_2)_4]$	2.279(2), 2.345(2)	[162]
$Y(DAC)[N(SiMe_3)_2]$	2.28(1), 2.29(2)[a]	[140a]
$Y(DAC)[CH(SiMe_3)_2]$	2.26(2), 2.27(2)	[140b]
$\{Yb[N(SiMe_3)_2]_2(\mu\text{-}DAC)\}_2Yb$	2.34(3)–2.41(3); 2.50(3)–2.61(3)[b]	[140a]
$\{[Cp^*SiMe_2(NtBu)]Sc(PMe_3)\}_2(\mu\text{-}C_2H_4)_2$	2.071(6)	[164]
$\{[Cp^*SiMe_2(NtBu)]Sc\}_2(\mu\text{-}C_3H_7)_2$	2.083(5)	[164]
$Y[N(SiMe_2CHPMe_2)(SiMe_2CH_2PMe_2)][N(SiMe_2CH_2PMe_2)_2]$	2.256(7), 2.396(7)	[168]
$\{Y(\eta^3\text{-}C_3H_5)[N(SiMe_2CH_2PMe_2)_2]\}_2(\mu\text{-}Cl)_2$	2.292(4)	[169]
$Nd[Me_2Si(OtBu)(NtBu)]_3$	2.398(5), 2.417(5), 2.387(5)	[171]
$[Me_2Si(OtBu)(NtBu)]_2Yb(\mu\text{-}Cl)_2Li(THF)_2$	2.247(5), 2.225(5)	[171]

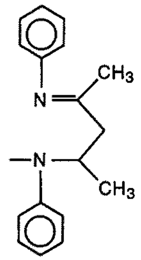
[a] Y–N(DAC) bond lengths

[b] Yb–N(DAC) distances to the central Yb are shorter

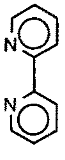
5.2 Sophisticated Ligand Systems



tBuDAB



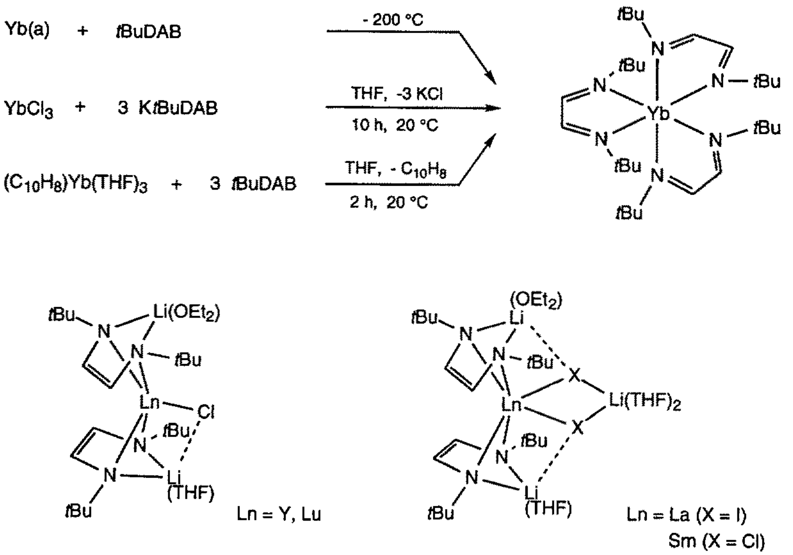
AIP



BiPy

The 1,4-diazabutadiene ligand *t*BuDAB can act both as radical anionic and dianionic chelating ligand. At first homoleptic lanthanide complexes of type Ln(*t*BuDAB)$_3$ have been prepared via metal vapor synthesis [172] (Scheme 9, Table 11). The formally lanthanide(0) complexes are best described as metal(III) complexes, Ln^{3+} (*t*BuDAB$^{\bullet -}$)$_3$, based on structural and ESR data. This is also consistent with the strong electropositive character of the lanthanide metals. Three *t*BuDAB ligands adopt a distorted tetragonal bipyramidal arrangement around the metal center. Magnetic susceptibility measurements revealed two different species for the ytterbium derivative [174]. At low temperature (5–15 K) the Yb(II)-species Yb(*t*BuDAB$^{\bullet -}$)$_2$(*t*BuDAB) was postulated as the predominant compound whereas the high temperature form (80–300 K) was ascribed to Yb(*t*BuDAB$^{\bullet -}$)$_3$.

The radical anionic character of the 1,4-diazabutadiene ligand was further proven in the heteroleptic complex Cp^*_2Sm(*t*BuDAB), synthesized from the strong single electron transfer reagent SmCp^*_2(THF)$_2$ and the free ligand [173].



Scheme 9. Radical anionic and dianionic chelating bonding mode of the *t*BuDAB ligand

Table 11. Chelating moieties with close Ln–N contacts

Compound	Ln–N	Ref.
Sm(*t*BuDAB)$_3$	av. 2.42(2)	[172b]
Yb(*t*BuDAB)$_3$	2.40(5)–2.43(4)	[174]
Cp^*_2Sm(*t*BuDAB)	2.480(5), 2.489(5)	[173]
Lu[Li(*t*BuDAB)(Et$_2$O)][Li(*t*BuDAB)(THF)]Cl	2.212(3)–2.282(3)	[158c]
Sm[Li(*t*BuDAB)(THF)](μ-Cl)$_2$Li(THF)$_2$	2.420(5), 2.482(4)	[158c]
Sm(AIP)$_3$	2.442(8)–2.483(8)	[175]
Gd(AIP)$_3$	2.435(2)–2.446(2)	[175]
(AIP)GdBr$_2$(THF)$_2$	2.366(7), 2.366(8)	[175]
Cp^*_2Sm(BiPy)	2.427(2), 2.436(2)	[99]
[Cp^*_2Y]$_2$[μ-η^2:η^2-OC(NC$_5$H$_4$)$_2$]	2.344(9), 2.348(9)	[177a]
[Cp^*_2Sm][μ-η^4-(PhN)OCCO(NPh)]	2.49(1)	[176a]
[Cp^*_2Sm][μ-η^4-(C$_5$H$_4$N)CH=C(O)C(O)=CH(C$_5$H$_4$N)]	2.473(7)	[176b]
Cp$_2$ScL[a]	2.133(7)	[177b]

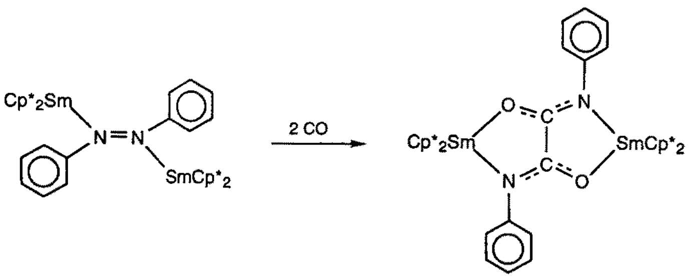
[a] L is shown in Scheme 10

^{13}C-NMR and Sm-C(Cp*) bond lengths strongly suggest the formation of a Sm(III) species. Analogous THF replacement and electron delocalization onto the ligand was observed in the reaction with constitutionally very similar bipyridine [99]. Again structural and spectroscopic data confirm the formation of a bipyridyl monoanion. Yb(*t*BuDAB)$_2$ has been generated from (C$_{10}$H$_8$)Yb(THF)$_3$ [174].

The dianionic form was discussed as an alternative, auxiliary coordination sphere [158c]. The structural features of LiCl adduct formation prevailing in heteroleptic complexes (Scheme 9) reflect the different size of the lanthanide centers. One *t*BuDAB ligand of each complex is involved in short Ln···C(olefin) contacts pointing out significant π-interaction and η^4-coordination (Lu-C: 2.643(4), 2.659(4), Sm-C: 2.654(6), 2.681(6) Å). ^{1}H NMR spectroscopy reveals dynamic behavior of the *t*BuDAB ligands in solution at ambient temperature. A similar heterometallic bridging moiety, Ln(μ-*t*BuDAB)Li, was observed in [Cp_2Yb(μ-*t*BuDAB)Li(DME)] [158b]. [CpYb(*t*BuDAB)]$_n$, obtained from the reaction of $CpYbCl_2(THF)_3$ with K_2[*t*BuDAB] in THF, was reported to suffer Cp-exchange and THF-cleavage under these conditions [158a].

Homoleptic and heteroleptic complexes of the bischelating 2-phenylamino-4-phenylimino-2-pentene ligand [(AIP)H] were synthesized in the form of $Ln(AIP)_3$ (Ln = Sm, Gd) and $(AIP)GdBr_2(THF)_2$ [175]. The AIP ligand does not provide a stable environment for Sm(II). Instead, the homoleptic Sm(III) derivative was obtained by the putative "$Sm(AIP)_2$" synthesis.

Sm(II) mediated formation of very sophisticated chelating ligands has been observed. The powerful reducing agent "Cp^*_2Sm" can induce facile double bond insertion of CO into C=C and C=N double bonds (Eq. 13) [176]. Carbon monoxide also inserts into the Y-pyridyl bond of Cp^*_2Y(2-pyridyl) to form a bridging μ-η^2:η^2-dipyridyl ketone fragment (Eq. 14) [177].



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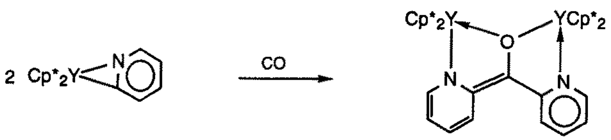
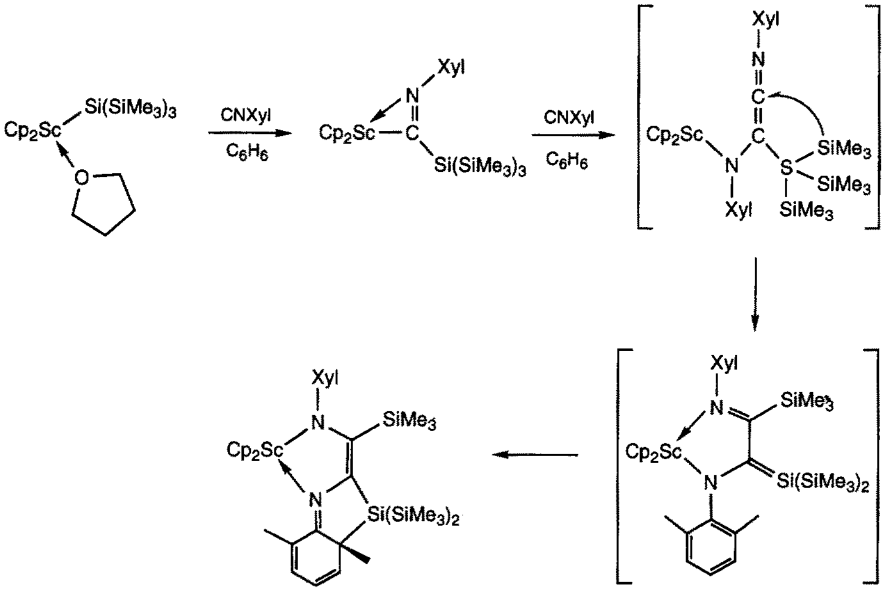


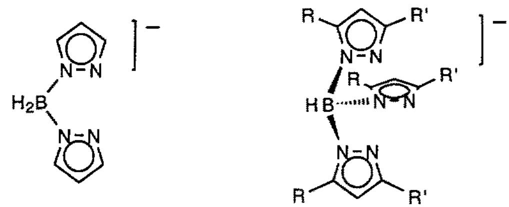
(14)

A "Sc-$Si(SiMe_3)_3$"-moiety mediates the insertion and coupling reactions of the isocyanide CN(Xyl)(Xyl = $C_6H_3Me_2$-2,6) (Scheme 10) [177b]. The mono-insertion product, yellow η^2-iminosilaacyl, could be isolated and charaterized. Addition of a second equivalent of substrate results in isocyanide coupling and further rearrangements to yield a final chelating moiety which contains a Sc-N σ-bond linkage. The rapid intramolecular rearrangement reactions probably proceed via a reactive silene intermediate.



Scheme 10. Formation of a Sc–N σ-bond by isocyanide insertion and coupling reactions

5.3 Polypyrazolylborate Ligands



TpR,R'

R, R' = H, Me, *t*Bu, 2-pyridyl

Polypyrazolylborate ligands are powerful chelating monoanionic ligands which form their closest metal contacts through the nitrogens of the pyrazolyl moiety [178, 179]. Interactions with lanthanide cations lie between Ln–N σ-bonds and Ln–N(donor) bonds (Tables 12 and 13). As their cyclopentadienyl counterparts the tripodal polypyrazolylborato ligands are accessible to steric fine-tuning mainly via substitution of the pyrazolyl group. For lanthanide complexation they have been used in the "6-electron donating" $[RBpz_3]^-$ (Tp) and the "4-electron donating" $[R_2Bpz_2]^-$ form.

5.3.1 Homoleptic Complexes

Anhydrous $LnTp_3$ precipitates from aqueous solutions by interaction of $LnCl_3$ with KTp (1:3) [180]. The molecular structure of the ytterbium derivative

Table 12. Homoleptic polypyrazolylborate complexes

Compound	Ln–N	Ref.
$YbTp_3$	2.401(9)–2.484(8), 2.544(7), 2.601(6)	[180a]
$Y(H_2Bpz_2)_3$	2.378(6)–2.396(5)	[181a]
$Sm[H_2B(pzMe_2\text{-}3,5)_2]_3$	2.510(7)–2.566(8)	[181c]
Sm(Tp-Me, Me)$_2$	2.617(4)	[183]
Yb(Tp-Me, Me)$_2$	2.480(4)	[184]

Table 13. Heteroleptic polypyrazolylborate complexes

Compound	Ln–N	Ref.
$Tp_2YCl(H_2O)$	2.460–2.516	[185]
$Tp_2YCl(Hpz)$	2.456(5)–2.546(4)	[186]
$CeTp_2(acac)$	2.583(3)–2.664(3)	[187]
$YbTp_2(acac)$	2.44(1)–2.58(1)	[187]
$YbTp_2(trop)$	2.43(1)–2.55(1)	[189]
$YbTp_2(O_2CPh)$	2.363(6)–2.481(6)	[189]
$[SmTp_2(\mu\text{-}O_2CPh)]_2$	2.45(2)–2.65(2)	[190]
$[YbTp(\mu\text{-}O_2CMe)_2]_2$	2.465(6)–2.488(6)	[186]
[Yb(Tp-Me,Me)$_2$][O_3SCF_3]	2.304(5), 2.347(6)	[184]
[Eu(Tp-Py)F(HOMe)$_2$][PF_6]	2.49(1)–2.55(1)	[192]
Yb(Tp-*t*Bu,Me)I(THF)	av. 2.458(8)	[194]
Yb(Tp-*t*Bu,Me)I(3,5-lutidine)$_x$	av. 2.45(3)	[194]
Yb(Tp-*t*Bu,Me)[$N(SiMe_3)_2$]^a	av. 2.46(2)	[151]

^{a} Ln–$N(SiMe_3)_2$ distance see Table 9

reveals 8-coordination of the metal center. Two trischelating and one bischelating ligands generate a bicapped trigonal prismatic coordination geometry [180a]. The sterically less crowded $[H_2Bpz_2]^-$ ligand exhibits a more regular, although more fancy, coordination chemistry. In $Y(H_2Bpz_2)_3$ six Y–N contacts build up a trigonal prism, where three rectangular faces are capped by bridging B–H···Y three center bonds [181a]. These interactions have been defined by short Y–B distances (av 3.211 Å), low B–H stretching bonds in the IR, nonequivalence of the BH_2-resonances in low temperature NMR spectra and a luminescence study of the terbium derivative [181b]. Similar structural features were observed in $Sm[H_2B(pzMe_2\text{-}3,5)_2]_3$ [181c].

The polypyrazolylborate ligand also provides a stabilizing environment for lanthanide(II) ions including Sm(II) [182–184]. Ln(Tp-Me,Me)$_2$ are remarkably insoluble and have crystallographically-imposed S_6-3-symmetry. The Sm derivative reacts with excess azobenzene to yield a more soluble 1:1 adduct [183]. The original η^3-bonding mode of the polypyrazolylborate ligand is retained, which documents a remarkable steric flexibility in the "solvent free" starting compound.

5.3.2 Heteroleptic Complexes

"Cp_2Ln–Cl"-analogous complexes have been prepared by starting both from hydrated and anhydrous lanthanide chlorides [179, 185]. The Y–Cl bond lengths in "monomeric" $YTp_2Cl(H_2O)$ is 2.657 Å, but IR data indicate intermolecular hydrogen bonding between H_2O and Cl ligands [185]. IR data also indicate intramolecular hydrogen bonding between Cl and the pyrazolyl hydrogen in $YTp_2Cl(Hpz)$ (Y-Cl: 2.721(2)) [186].

The chloride complexes served as precursors in numerous syntheses of heteroleptic systems containing O,O-bischelating ligands (Table 13: diketonates, troponolates, carboxylates) [187–190]. The synthesis of these complexes occurred as a reflection of the η^2-coordination of one Tp ligand in the homoleptic system $LnTp_3$. Unlike the homoleptic complexes which are stereochemically rigid on ^1H NMR time-scale [180b], the heteroleptic complexes undergo intramolecular ligand reorganization processes which are rapid on the ^1H NMR time-scale down to at least −80 °C. Intermolecular ligand exchange, which determines disproportionation reactions, was found to be slow [191]. Complexes of the large lanthanide ions become both more insoluble and unstable by reducing the O,O-chelate ring from six (acac) to four (carboxylate) [189]. In the presence of carboxylate ligands dimeric complexes have also been isolated [186, 190]. Well separated $[Yb(Tp\text{-}Me,Me)_2]^+$ cations and $CF_3SO_3^-$ anions were found in $Yb(Tp\text{-}Me,Me)_2(O_3SCF_3)$ [184].

The heteroleptic fluoride complex $[Eu(Tp\text{-}Py)F(HOMe)_2][PF_6]$ was formed in the reaction of KL with $EuCl_3 \cdot 6H_2O$ in methanol and subsequent addition of KPF_6 [192]. Pyridyl groups in 3-position of the pyrazole rings of the borate ligand provide an efficient shielding of the metal center. Six coordination sites of a mono-capped square antiprismatic coordination polyhedron are occupied by this expanded tripodal ligand. Mixed Ln(COT)(Tp) complexes have also been reported [193].

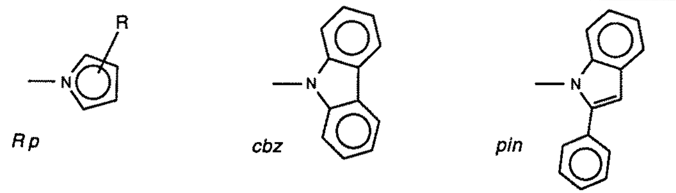
Half-sandwich pyrazolylborate complexes of ytterbium(II), Yb(Tp-*t*Bu,Me)I $(L)_x$ (L = THF: x = 1; L = (3,5-lutidine): x = 2) provided a suitable precursors for the synthesis of mixed ligand "LLnR" type complexes with R = $N(SiMe_3)_2$, μ-$HBEt_3$, $CH(SiMe_3)_2$, CH_2SiMe_3 [151, 194]. The Yb–I bonds of the monomeric precursor complexes fall in the range of 3.0536(8)–3.123(1) Å. The Yb–$N(SiMe_3)_2$ and Yb–$CH(SiMe_3)_2$ moieties show short Yb···$C(SiMe_3)$ contacts of 3.064(5) and 3.08 Å, respectively.

6 Complexes with Unsaturated Heterocyclic Ligands

Unsaturated heterocyclic ligands like pyrrols or porphyrins are formally derived from secondary organic amines and their metal derivatives are therefore amide complexes. The Ln–N σ-bond lengths formed with simple monocyclic ligands are comparable to those observed in alkyl and silylamides. Monocylic ligands are also able to form η^5-coordinated metal complexes and are handled as alternative spectator ligands to the isoelectronic, ubiquitous cyclopentadienyl ligand. All monocyclic lanthanide complexes are moisture sensitive. Macrocyclic ligands like phthalocyanins or porphyrins offer another attractive rigid ligand frame to metal centers which resembles the COT ligand. These so-called "equatorial templates" impose steric, conducting, electrochromic and opto-electronic properties which are promising for various applications.

6.1 Five-Ring Ligands

6.1.1 Pyrrole and Carbazole Ligands (Table 14)



R = H; Me_2-2,5; *t*Bu_2-2,5; Ph_4-2,3,4,5

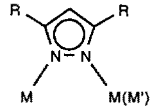
Pyrrole ligands can form both Ln–N σ-bonds and η^5-π-Ln bonds. σ-Bonds have been observed in heteroleptic lanthanide(III) complexes with sterically less crowded pyrrole ligands [195]. The introduction of sterically demanding groups in α-position as in 2,5-di-*tert*-butylpyrrole led to a shielding of the nitrogen and subsequent η^5-coordination to the lanthanide center [196]. Additionally, η^1-coordination to a sodium atom is observed in the obtained *ate* complex.

In lanthanide(II) carbazole complexes of type $Ln(cbz)_2(solvent)_4$ Ln–N σ-bonds can even stabilize samarium(II) [197, 198].

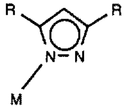
Table 14. Structurally characterized lanthanide pyrrole and carbazole complexes

Complex	d(Ln-N) [Å]	Ref.
$Cp_2Lu(dmp)(THF)$	2.289(4)	[195]
$(dtBup)_2Nd(\mu\text{-}Cl)_2[Na(THF)_2]$ $(\mu\text{-}Cl)_2Nd(dtBup)_2$	2.791(3), 2.720(3)	[196]
$Eu(cbz)_2(THF)_4$	2.545(5), 2.572(5)	[197b]
$Sm(cbz)_2(THF)_4$	2.547(3), 2.583(3)	[198]
$Sm(cbz)_2(N\text{-}MeIm)_4$	2.587(6), 2.597(16)	[198]

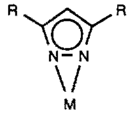
6.1.2 Pyrazole Ligands (Table 15)



A



B



C

R = H, Me, *t*Bu, Ph

Table 15. Structurally characterized lanthanide pyrazole complexes

Complex	d(Ln-N) [Å]	Ref.
$[Nd(dmpz)_3(THF)_2]_2$	terminal: 2.400(2)–2.426(3) bridging: 2.509(2), 2.511(2)	[199]
$Y_3(\mu\text{-dmpz})_6(\mu_2\text{-dmpz})_3(\mu_3\text{-O})Na_2(THF)_2$	terminal: 2.275(5)–2.348(5) bridging. 2.402(4)–2.476(4)	[200a]
$Ho_3(\mu\text{-dmpz})_6(\mu_2\text{-dmpz})_3(\mu_3\text{-O})Na_2(Hdmpz)_2$	terminal: 2.307(3)–2.391(3) bridging: 2.437(3)–2.567(4)	[200a]
$[O(CH_2CH_2C_5H_4)_2Y]_2(\mu_2\text{-dmpz})(\mu\text{-OH})$	2.445(5)	[200b]
$Nd(t\text{Bu}_2pz)_3(THF)_2$	2.381(8)–2.492(9)	[201a]
$Er(t\text{Bu}_2pz)_3(THF)_2$	2.274(7)–2.386(8)	[201b]
$[Er(Ph_2pz)_3(OPPh_3)_2](DME)$	2.33(1), 2.32(2), 2.37(1)	[202]
$[Nd(Ph_2pz)_3(THF)_3](THF)$	2.420(10)–2.524(8)	[202]

Pyrazole ligands are of interest due to their different coordination behavior to metal centers [199–202].

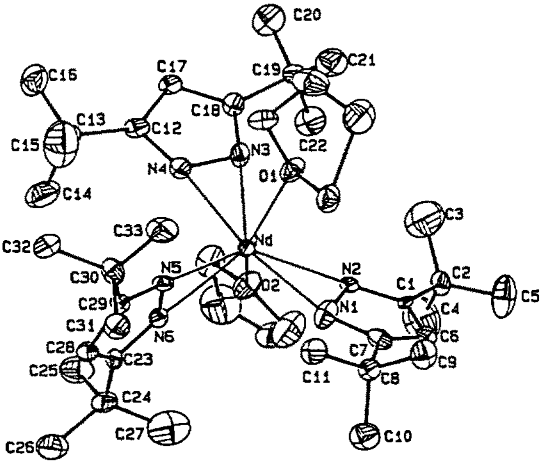
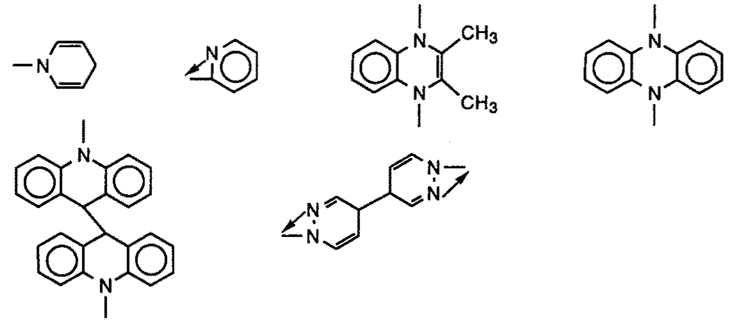


Fig. 19. ORTEP view of $Nd(t\text{Bu}_2pz)_3(THF)$ [201a]

Lanthanide derivatives bear structural evidence for type A (μ-η^2-bridging) and type C (η^2-terminal) coordination. In dimeric complexes with 3,5 dimethyl substituted ligands both coordination modes are present [199]. Use of more bulky 3,5-di(*t*butyl)pyrazole and 3,5-di(phenyl)pyrazole ligands results in monomeric species with only η^2-bonding (Fig. 19) [201, 202]. These complexes undergo proteolytic exchange reactions comparable to the silylamides. Unsubstituted pyrazole complexes are considered to be polymeric with additional η^5- and μ-η^2-bonding or η^5- and μ-η^5-η^1-bonding [199].

6.2 Six-Ring Ligands



In the course of probing the range of reactivity accessible to decamethylsamarocene, substrates containing C=N double bonds as part of 6-membered heterocycles have been tested. In the reaction with pyridazine reductive carbon–carbon bond formation occurred (compare Sect. 3.2) [99]. The coupled ligand bridges two Sm(III) centers via the four nitrogen positions. In the phenazine reaction one phenazine ligand is placed between the Sm(III) centers (Fig. 20; Table 16) [203].

The structure resembles the corresponding anthracene complex [203]. The ligand is bonded in an allylic fashion with Sm–N bonds in the range of Ln–N σ-bonds and Ln–C bonds at the long range end of allylic interactions (2.866(3), 2.877(2) Å). In contrast the reaction of SmCp$^*_2$ with acridine again yielded a coupled product, which contains a similar allylic bonding pattern (Sm–C, 2.944(5), 2.970(5) Å) [203].

Fused heterocyclic dianionic ligands are also accessible to lanthanide(III) complexes which has been shown for quinoxaline and phenazine [204] (Table 16). The existence and availability of the alkali metal precursors allows the usual metathesis reaction.

Reaction of Cp*LuH with pyridine yielded the orthometallated (C,N-η^2) pyridine complexes under release of hydrogen [205]. The scandium complexes Cp$^*_2$ScR (R = H, CH_3, C_6H_5, $CH_2C_6H_5$) show a similar reaction [206].

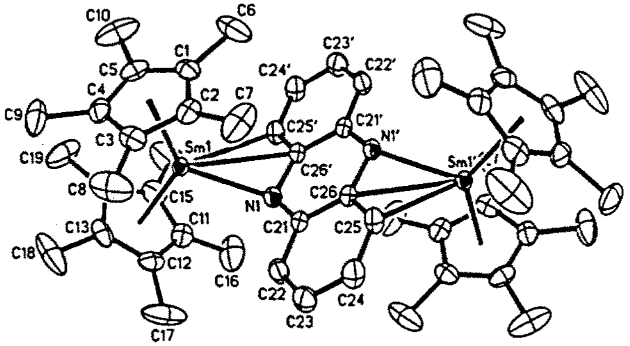


Fig. 20. ORTEP view of $[Cp^*_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{12}H_8N_2)]$ [203]

Table 16. Ln–N bonds lengths involving 6-ring heterocyclic systems

Complex	d(Ln–N) [Å]	Ref.
$[Cp^*_2Sm]_2[\mu\text{-}\eta^4\text{-}(CH{=}NNCH{=}CHCH\text{-})_2]$	2.351(6), 2.430(6)	[99]
$[Cp^*_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{12}H_8N_2)]$	2.360(2)	[203]
$[Cp^*_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{13}H_9N)]$	2.380(5)	[203]
$[Cp^*_2La]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_8H_4N_2\text{-}2,3\text{-}Me_2)]$	2.409(4), 2.444(4)	[204]
$[Cp^*_2La]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}(C_{12}H_8N_2)]$	2.452(2)	[204]
$Cp^*_2Sc(C,N\text{-}\eta^2\text{-}Py)$	2.14[a]	[206]

[a] Estimated value because of disordering

6.3 Macrocyclic Ligands

Complexation of macrocyclic ligands to lanthanide cations has been studied extensively [207, 208]. One main reason for the current interest in those macrocyclic complexes are their intrinsic paramagnetic and luminescent properties. There is also the steadily increasing number of tailor-made macrocyclic ligands [209]. This section will focus on complexes which contain macrocycles as discrete counterions and in particular on the coordination chemistry of phthalocyanine (Pc) and porphyrin (Por) ligands. Schiff base ligands which display another source of amine functionalities are usually not deprotonated under the prevailing reaction conditions [210].

Sandwich and triple-decker complexes are routinely observed for Por and Pc ligands and have attracted most attention (Fig. 21; Buchler, Weiß). The sandwich systems are thermally stable and sublimable and show only limited moisture sensitivity. The lanthanide cations are located between two saucer-shaped macrocycles usually forming a square antiprismatic coordination polyhedron. The separation of the two macrocyclic rings is very close, starting at

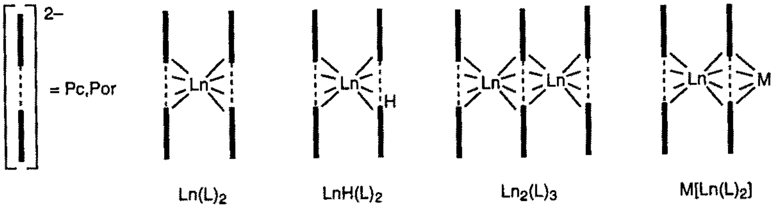
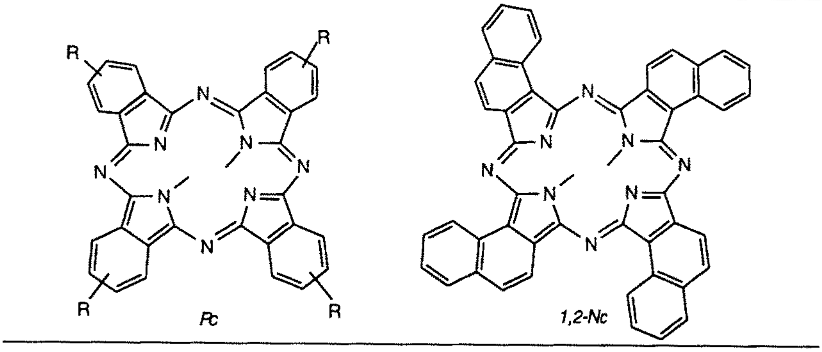


Fig. 21. Routinely observed constitutions of lanthanide Pc and Por complexes

2.7 Å depending on the size of the lanthanide metals. Delocalization of electron density on four equivalent nitrogen atoms causes elongation of the Ln–N bonds at about 0.10–0.15 Å compared to silylamides. The close proximity of the macrocyclic π-systems in sandwich complexes proved to be useful as structural and spectroscopic models for the bacteriochlorophyll $[Mg(Bchl)]_2$, the "special pair" in the reaction center of bacterial photosynthesis [211, 212]. The distance between the pyrrole rings in $[Mg(Bchl)]_2$ is about 3 Å.

6.3.1 Phthalocyanine Ligands



R = H, Me, *t*Bu, OMe

Since the pioneering work of Kirin et al. [5] various lanthanide(III) and cerium(IV) complexes containing phthalocyanine ligands have been synthesized (Table 17) [213–221]. Equations 15a, b give typical methods of preparation for Ln(III) derivatives.

$$\text{exc.}(CN)_2C_6H_4 + Lu(OAc)_3 \cdot H_2O \xrightarrow{\text{cyclohexanol, DBU, } \Delta} Lu(Pc)_2 + 3HOAc$$

$$\text{DBU} = \text{1,8-diazabicyclo[5.4.0]undec-7-ene} \qquad (15a)$$

$$2Li_2Pc + Lu(OAc)_3 \cdot H_2O \xrightarrow{\text{chloronaphthalene}} Lu(Pc)_2 + 3LiOAc \qquad (15b)$$

The second route has been developed for derivatives with two differently substituted Pc ligands [218]. Ce(IV)Pc_2 could not be synthesized according to

Table 17. Ln–phthalocyanine complexes

Compound	d(Ln-N)	d(Ln-N$_4$)^a	Ref.
α-[Pr(Pc$^-$)$_2$]Br$_{1.5}$	2.50(1), 2.60(1)	1.62	[213b]
α-[Pr(Pc^{2-})(Pc$^-$)]	av. 2.522(6), av. 2.625(6)	–	[217a]
α-Nd(Pc)$^{2-}$(Pc$^-$)]	av. 2.504(4), av. 2.15(4)	–	[217b]
β1-[Pr(Pc^{2-})(Pc$^-$)]	2.400(2)–2.539(2)	1.50	[217c]
β-[Nd(Pc^{2-})(Pc$^-$)]	av. 2.470(4)	1.47	[217d]
γ-[Lu(Pc^{2-})(Pc$^-$)]	2.34(2)–2.41(2)	1.33, 1.35	[217e]
[Y(Pc^{2-})(Pc$^-$)]·CH$_2$Cl$_2$	2.395(3)–2.406(4)	1.380	[216b]
[Lu(Pc^{2-})(Pc$^-$)]·CH$_2$Cl$_2$	2.369(5)–2.392(7)	1.34, 1.35	[216a]
Ce(Pc^{2-})$_2$	2.399(6)–2.426(7)	1.38	[213a]
Nd(Pc^{2-})$_2$H·CH$_2$Cl$_2$	2.39–2.49	–	[214]
Lu(Pc^{2-})$_2$H	2.359(5)–2.389(7)	1.337, 1.339	[215]
[Lu(Pc^{2-})$_2$[N*n*Bu$_4$]·2DMF	2.366(3)–2.407(3)	1.334, 1.367	[215]
[La(Pc^{2-})$_2$][PNP]·2DMF	2.529(9)–2.569(8)	–	[213c]
[Gd(Pc^{2-})$_2$][PNP]·0.3H$_2$O	2.433(6)–2.453(7)	–	[213c]
[Tm(Pc^{2-})$_2$][PNP]·0.5H$_2$O	2.392(8)–2.412(8)	–	[213c]
Sm$_2$(Pc^{2-})(thd)$_4$	av. 2.66(2)	–	[218]
Lu(Pc^{2-})(OAc)(H$_2$O)$_2$·H$_2$O·2CH$_3$OH	2.333(3)–2.359(3)	1.26	[216a]

[a] Distance from the mean plane of four coordinating nitrogens

this procedure due to the reducing reaction conditions [213a]. Instead, anodic or chemical oxidation of the Ce(III) species with dibenzoyl peroxide has been successful [216]. The isolation of such complexes revealed that sole nitrogen counterion coordination can stabilize cerium(IV). The blue and green lanthanide compounds which are formed according to Eq. (15a) have been subjected to numerous investigations [214–217, 220]. The characterization of both compounds succeeded in the case of lutetium including X-ray structure determination. The green form was identified as the one electron ligand-oxidized, non-protonated [Lu(Pc^{2-})Pc$^-$)] (Fig. 22) [216a]. The blue compound was defined as the reduced, protonated LuHPc$_2$ [215].

Polymorphism has been detected in the oxidized diphthalocyanine derivatives [Ln(Pc^{2-})(Pc$^-$)] [217]. Three different modifications (α, β, γ) could be generated via electrochemical methods. The structural differences are especially caused by the molecular packing which is expressed in the shortest intermolecular distances of the monoclinic β- and the orthorhombic γ-phase (C···C: γ-[Lu(Pc^{2-})(Pc$^-$)] 3.18 Å [217e], β-[Nd(Pc^{2-})(Pc$^-$)] 3.48 Å [217d]). Both in the β- and γ-phase the pyrrole and benzene rings are tilted to result in a saucer-shaped Pc-ligand and a biconcave lens shaped molecule, respectively. Already in the β1-phase of praseodymium this structural feature is partly omitted due to differently oriented ring moieties [217c]. The β-phase forms a layer structure with parallel π-electron systems. In the tetragonal α-phase the molecules lose their individual character to form infinite molecular columns with almost planar, propeller-like Pc-ligands [217a, b].

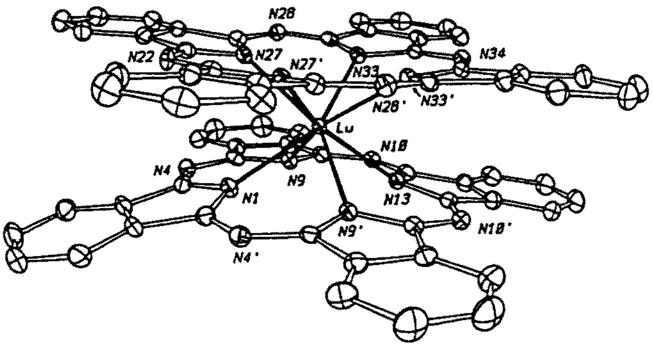


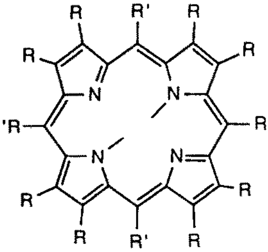
Fig. 22. Molecular structure of $Lu(Pc^{2-})(Pc^{-})$ [216a]

Complexes containing two ring-oxidized Pc-ligands were obtained both by electrochemical and chemical methods [213b]. The brownish red complexes of variable composition, $[Pr(Pc^{-})_2]X_y$ ($X = Br$, $y = 1 \leq y \leq 2.5$) release halogen under reduced pressure and at temperatures > 250 °C to yield α-$[Pr(Pc^{2-})(Pc^{-})]$. The solid state structure of $[Pr(Pc^{-})_2]Br_{1.5}$ reveals elongated Ln-N bond distances and almost planar Pc-ligands as a result of decreased electrostatic attractions. Disordered Br^- and Br^{3-}, located in the $[Pr(Pc^{-})_2]^+$-channel arrangement accomplish charge balance. The deviation of planarity (increase of saucer-shape) in the ordering $[Ce(Pc^{2-})_2] > [Ln(Pc^{2-})(Pc^{-})] > [Pr(Pc^{-})_2]X_y$ is commonly associated with increased repulsion of the opposite π-electron systems.

Electronic and steric cation-anion interactions in complexes of type $[L^+][Ln(Pc^{2-})_2]$ also affect the packing of the two staggered phthalocyanine rings, as evidenced in an unsymmetrical funnel-shape for $L^+ = PNP$ (PNP = bis(triphenylphosphine) iminium) [213c].

The formation of triple-decker complexes has been mentioned [221] including the 1,2-napthalocyaninato complex $Lu_2(1,2\text{-}Nc)_3$ [222]. Homoleptic $Lu(2,3\text{-}Nc)_2$ and heteroleptic Lu(2,3-Nc)(Pc) have been prepared according to Eq. (15b) [223]. The heteroleptic complex $Pc[Sm(thd)_2]_2$ has been prepared by reacting $Sm(thd)_3$ with Li_2Pc [218].

6.3.2 Porphyrin Ligands



Por

Structurally characterized Ln(Por)-complexes:
R' = H, R = Et: OEP, 2,3,7,8,12,13,17,18-octa(ethyl)porphyrin;
R = H, R' = Ph: TPP, mesotetra(phenyl)porphyrin;
R = H, R' = Tol: TTP, mesotetra(tolyl)porphyrin;
R = H, R' = C_6H_4-4-OMe: T(4-OCH_3)PP, mesotetra(anisyl)porphyrin

Porphyrin complexes were first sythesized in 1971 [224] and further studied in 1974 with a view to exploit a new class of lanthanide shift reagents [225]. Publication of the intrinsic properties of the phthalocyanine counterparts shed new light on this class. While the study of the phthalocyanine complexes was hampered by their low solubility the Por analogues are generally more accessible to a wider range of solvents, thus leading to improved crystallization conditions [226]. To optimize the crystallization behavior a couple of substituted porphyrins have been examined (Table 18) [226–234].

Scheme 11 shows the standard route to lanthanide porphyrin complexes [24, 235, 236]. Depending on the lanthanide metal all intermediates and products can be isolated via column chromatography on alumina.

Double-decker complexes of the smaller elements (Tb–Lu) [237] are available by activated Por-precursors, namely Li_2Por [238]. Lanthanide dialkylamides should provide an alternative route [239]. Triple-decker complexes are more readily formed compared to the Pc derivatives (Fig. 23). In an effort to force the localization of the unpaired electron on one ring, heteroleptic systems such as Por/Por′ and Pc/Por lanthanide sandwich complexes have been studied (Table 18; Fig. 23).

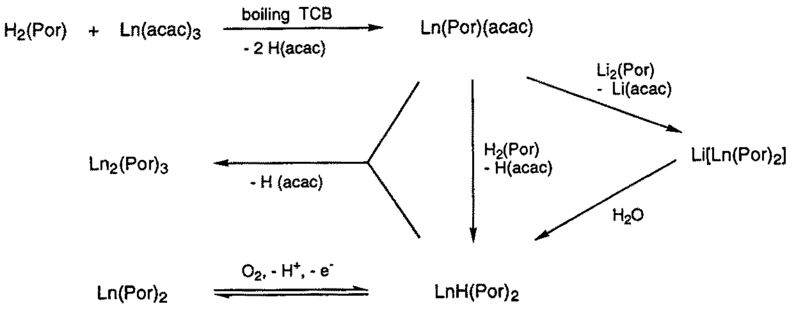
Table 18. Ln-porphyrin complexes[a]

Compound	d(Ln-N)[b]	d(Ln-N₄)[c]	Ref.
$Ce(OEP)_2$	2.467(3)–2.484(3)	1.375, 1.377	[226a]
$Ce_2(OEP)_3$	2.481(4)–2.523(4)	1.394	[226a]
	2.745(4)–2.768(4)	1.876	
$Eu(OEP)_2$	2.473(4)–2.556(4)	1.415, 1.433	[227]
$Tl[Pr(OEP)_2]$	2.48(16), 2.64(9)	1.36, 1.69	[228]
SmH(OEP)(TPP)	Sm–N(OEP) 2.563(4)	1.516	[229]
	Sm–N(TPP) 2.538(4)	1.470	
Ce(OEP)(TPP)	Ce–N(OEP) 2.471(1)	–	[230]
	Ce–N(TPP) 2.480(1)	–	
$Nd_2(Pc)_2[T(4\text{-}OCH_3)PP]$	Nd1-Por 2.47(2)	1.294	[231]
	Nd1-Pc1 2.74(2)	1.966	
	Nd2-Pc1 2.57(2)	1.722	
	Nd2-Pc2 2.43(2)	1.364	
$Ce(Pc)[T(4\text{-}OCH_3)PP]$	Ce–Por 2.434(7)	1.314	[232]
	Ce–Pc 2.465(7)	1.466	
$[Ce(TPP)(Pc)][SbCl_6]$	Ce–TPP 2.420(2)	–	[232]
	Ce–Pc 2.458(2)	–	
$(TPP)Ce[Pc(OCH_3)_8]Ce(TPP)$	Ce–N(TPP) 2.469(3)	1.353	[233]
	Ce–N(Pc) 2.721(3)	1.922	
$(Pc)Ce[T(4\text{-}OCH_3)PP]Ce(Pc)$	Ce–N(Pc) 2.473(2)	1.470	[233]
	Ce–N(TPP) 2.727(2)	1.832	

[a] Solvent of crystallization is not reported in the formula

[b] Average distance or bond range

[c] Distance from the mean plane of four coordinating nitrogens



Scheme 11. Synthesis of lanthanide Por complexes

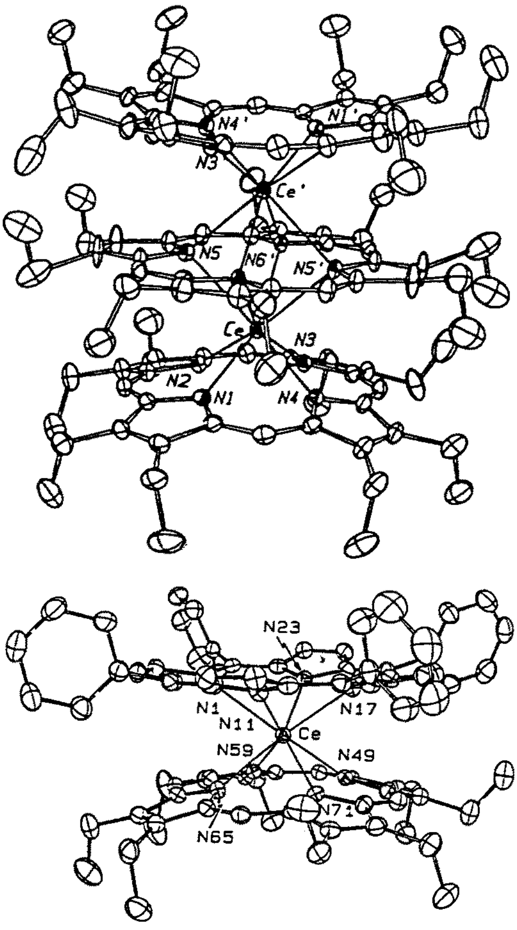


Fig. 23. Molecular structures of $Ce_2(OEP)_3$ [226a] and Ce(OEP)(TPP)[230]

Although LiPor-precursors are involved in the synthesis, *ate* complexes of type $M^I[LnPor_2]$ have not been isolated, in contrast to the pyrrol derivatives [197] or charge related $M^I[Ln(COT)_2]$ complexes [240]. However, ternary systems are readily available by reaction of the protonated form $HLnPor_2$ with, e.g., M^IOR (Eq. 16). Structural evidence has been given for the thallium complex $Tl[Pr(OEP)_2]$ [228].

$$HPr(OEP)_2 + TlOEt \rightarrow Tl[Pr(OEP)_2] + HOEt \qquad (16)$$

Use of Por ligands as stabilizing co-ligands in lanthanide complexes containing reactive Ln–X bonds (Table 19) requires different methods of preparation. For scandium the important heteroleptic complex ScPorCl has been readily available from both the reaction of anhydrous $ScCl_3$ with $PorH_2$ and $ScCl_3(THF)_3$ with Li_2Por [241]. The structure analysis revealed a monomeric, square pyramidal configuration with a very short Sc–Cl bond of 2.32(1) Å. Subsequent standard metathesis reactions with M^IR ($R = Me$, $CH(SiMe_3)_2$, CH_2CMe_3, Cp, MeCp, Cp*, Ind, $N(SiMe_3)_2$, $OCMe_3$, $OSiMe_3$, $OC_6H_2Me_3$-2,4,6, OTf) can be applied to yield heteroleptic Sc(OEP)(R) including the mixed amide complex $Sc(OEP)[N(SiMe_3)_2]$ [242,243]. The derivatives of R = Cp, Ind, Me and $CH(SiMe_3)_2$ have been structurally defined as mononuclear species which on hydrolysis produce bright red bis(μ-hydroxide) dimer $[(OEP)Sc(\mu\text{-}OH)]_2$ [243].

A more elegant pathway starts from homoleptic LnR_3 ($R = CH(SiMe_3)_2$, $OC_6H_3tBu_2$-2,6) [244]. The molecular structure of $(OEP)Lu[CH(SiMe_3)_2]$ displays a square pyramidal coordination geometry at lutetium with a terminal Lu–C distance of 2.374(8) Å (Fig. 24, Table 19).

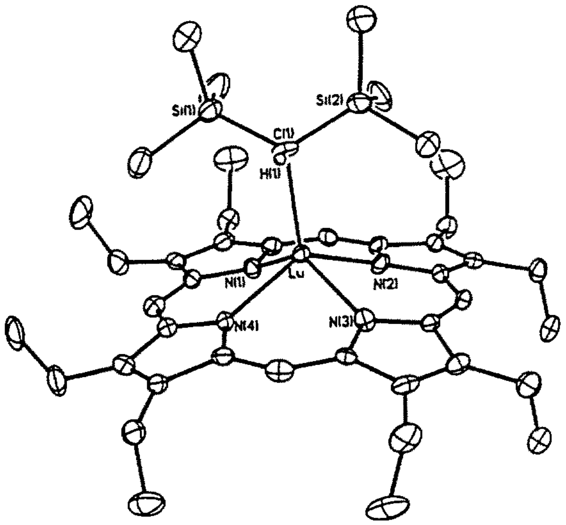


Fig. 24. ORTEP drawing of $(OEP)Lu[CH(SiMe_3)_2]$ [244]

Table 19. Ln-X-porphyrin complexes[a]

Compound	d(Ln-N)[b]	d(Ln-N_4)[c]	Ref.
ClSc(TTP)	2.17(3)–1.18(3)	0.68	[241]
O[Sc(TTP)]$_2$	2.15(3)–2.21(3)	0.82	[241]
Sc(OEP)Cp	2.184(3)–2.197(3)	0.80	[242]
Sc(OEP)Me	2.151(2)–2.158(2)	0.66	[243]
Sc(OEP)[CH(SiMe$_3$)$_2$]	2.142(6)–2.196(6)	0.71	[243]
Sc(OEP)Ind	2.170(6)–2.196(6)	0.78	[243]
[(OEP)Sc(μ-OH)]$_2$	2.195(2)–2.216(2)	0.84	[243]
Lu(OEP)[CH(SiMe$_3$)$_2$]	2.236(7)–2.296(7)	0.918	[244]

[a] Solvent of crystallization is not reported in the formula

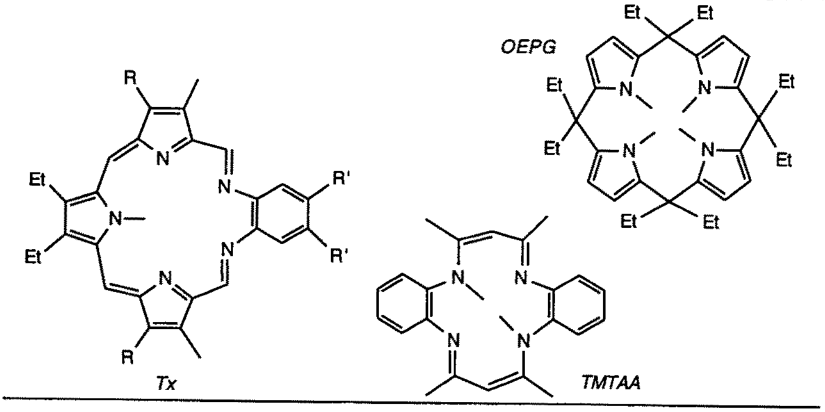
[b] Bond range

[c] Distance from the mean plane of four coordinating nitrogens

The alkyl derivative is a versatile starting material in protonolysis reaction, e.g., with HOAr or HC≡C*t*Bu. However, the formation of Ln(Por)[CH(SiMe$_3$)$_2$] underlies steric restrictions. For example, the lanthanum derivative could not be isolated. This fits into the overall picture of Ln-Por-complexes which are more stable for the late elements. Destabilization by larger lanthanide elements has also occurred in Ln(Por)(OAc) complexes. In addition, the formation of LnPor(R) is dependent on the substitution pattern of the Por ligand because tetratolyl-Por (TTPH$_2$) and tetramethyl-Por (TMPH$_2$) did not undergo this reaction.

(OEP)Y(μ-Me)$_2$AlMe$_2$, prepared via the (OEP)Y(OAr)/MeLi/AlMe$_3$-procedure [244], activates O_2 at room temperature to afford (OEP)Y(μ-OMe)AlMe$_2$. In contrast to cyclopentadienyl chemistry [245], the hard donor bonding and changed ligand geometry in (OEP)Ln[CH(SiMe$_3$)$_2$] prevent hydrogenolysis of the Ln–C bond.

6.3.3 Other Macrocyclic Ligands



Invariably hydrolytic instability of lanthanide Por complexes, particularly that observed for the larger lanthanide elements, negatively influences their prospective application in terms of biomedicine (Sect. 7.4). As a response to this problem, larger porphyrin-like or "expanded porphyrins", the so-called "texaphyrins" (Tx), have been examined by Sessler et al. [246]. The motivation, that expanded systems better accommodate larger ions, was previously demonstrated in a uranyl "superphthalocyanine" (SPc) complex [247]. This SPc-complex contains an expanded, cyclic five-subunit pentakis(2-iminoisoindoline) which is formed by a template reaction of *o*-dicyanobenzene with anhydrous uranyl chloride. The uranium is displaced by only 0.02 Å from the mean N_5-plane.

The central hole or binding core in texaphyrins is roughly 20% larger than that of the porphyrins and accomplishes pentadentate binding [247]. In the course of the studies to exploit coordination behavior with lanthanide cations a serious of monoanionic texaphyrine complexes have been synthesized and fully characterized (Eq. 17, Table 20) [248].

$$TxH_2 + Ln(NO_3)_3 \cdot H_2O \xrightarrow{NEt_3,\,HOMe} Ln(Tx)(NO_3)_2(H_2O)_y(HOMe)_z \qquad (17)$$

Due to the enhanced proximity of the lanthanide cations to the N_5-plane, 1:1 coordination results and double decker complexes were not observed. The Ln–N interactions display two closer and three longer bond lengths. The next coordination sphere is completed by alternating NO_3^--, H_2O- and HOMe-ligation depending on the metal. The effect of axial co-ligation was studied by ^{1}H NMR spectroscopic techniques. Both the number and type (nitrate or phosphate (Fig. 25)) of axial coligands drastically change the spectral pattern [249]. Indeed, LnTx complexes are water stable and the solubility can be controlled by functionalization of the macrocyclic ligand.

Meso-porphyrinogens formally represent the "structural transition" between pyrroles and porphyrins. Stimulated by the work of Floriani et al. [251], porphyrinogens were considered as alternative ligand sets in lanthanide chemistry by Jubb and Teuben [68, 252]. The tetraamide ligand offers a coordination environment which is obviously sterically and electronically more flexible than that provided by the standard Cp_2Ln–fragment. The conformational flexibility

Table 20. Ln–Tx complexes [248-250]

Ln	R	R′	Co-ligand	d(Ln-N)	d(Ln-N_5)[a]
La	Et	OMe	NO_3	2.484(5), 2.506(5); 2.615(4)–2.685(3)	0.914
Eu	$(CH_2)_3OH$	$O(CH_2)_3OH$	NO_3	2.388(3), 2.395(2); 2.500(2)–2.538(2)	0.606
Eu	$(CH_2)_3OH$	$O(CH_2)_3OH$	NO_3	2.383(4), 2.388(4); 2.494(4)–2.536(3)	0.595
Gd	Et	OMe	NO_3	2.401(5), 2.407(5); 2.517(4)–2.579(4)	0.694
Dy	Et	OMe	$PO_2(OPh)_2$	2.317(5), 2.335(5); 2.437(4)–2.459(4)	0.073
Lu	Et	$O(CH_2)_3OH$	NO_3	2.312(4), 2.324(4); 2.412(4)–2.455(4)	0.269

[a] Distance from the mean plane of five coordinating nitrogens

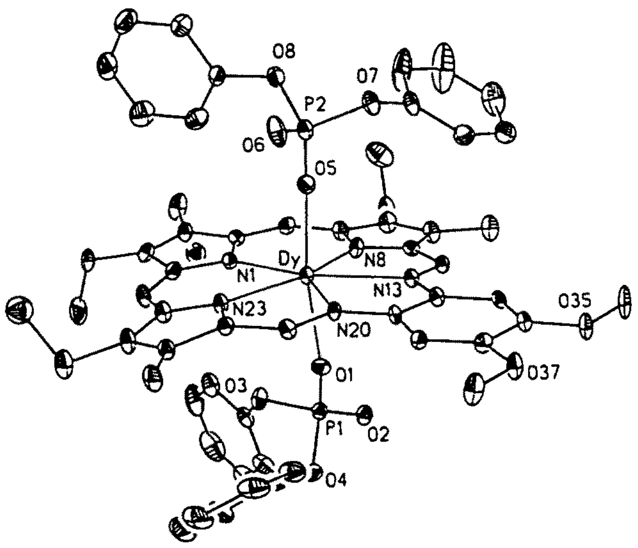


Fig. 25. Molecular structure of $Dy(Tx)[PO_2(OPh)_2]_2$ [249]

allows η^1-, η^3- or η^5-bonding to the metal center. Formation of *ate* complexes as in simple pyrroles is almost obligatory by starting with $(OEPG)[Li(THF)]_4$ and lanthanide chlorides. On the other hand, double- or triple-decker complexes as observed in porphyrin systems (previous section) are very unlikely due to the high charge density in the ligand.

Syntheses so far with lanthanide elements resulted in the formation of unpredictable compounds (Table 21). Reaction of $YCl_3(THF)_3$ and lithium porphyrinogen in THF yielded $[Li(THF)_2(OEPG)Y(\mu\text{-}OEt)Li(THF)]$ (Fig. 26) [252]. The metal bridging ethoxide is believed to arise from in situ cleavage of THF (Y–O, 2.144(2) Å). Subsequent reaction with either $LiCH(SiMe_3)_2$ or $LiBEt_3H$ did not lead to the formation of putative yttrium alkyl or hydride species, respectively. Instead "yttrium-free" component $[(OEPG)(LiTHF)_4]$ $[(THF)Li(OCH{=}CH_2)]_2$ could be isolated. A synthesis involving a Sm(II) species was discussed earlier as part of a different topic (Sect. 2.3) [67].

Alkali metals also play an active part in the formation of double- or triple-decker complexes of the macrocyclic ligand $[(TMTAA)H_2]$ (tetramethyl dibenzotetraaza[14]annulen) (Table 21). Reaction of $[Li_2(TMTAA)]$ with $CeBr_3$ yielded the *ate* double-decker complex $[Li(THF)][(TMTAA)_2Ce]$ [253a]. Cerium adopts an antiprismatic geometry and as expected forms longer bond lengths to the macrocycle where the lithium is participating (Table 21). Reaction of $SmI_2(THF)_2$ with the dipotassium salt of the ligand did not yield the putative Sm(TMTAA) [253b]. Instead the strongly reducing Sm(II) induced a complicated redox reaction and a polynuclear metal complex $[K(THF)_3]_2$ $[(TMTAT)_2Sm_2]$ was formed (TMTAT = tetramethyldibenzotetraazatetra-

Table 21. Macrocyclic complexes with Ln–N(amide) bonds

Compound	d(Ln-N)	d(Ln-N$_4$)	Ref.
$[(THF)_2Li(OEPG)Sm]_2(N_2Li_4)$	η^1: 2.340(3), 2.369(3), 2.337(3) η^5: 2.547(3)	–	[67]
$[Li(THF)_2(OEPG)Y(\mu\text{-}OEt)Li(THF)]$	η^1: 2.462(2), 2.502(3), 2.455(2) η^3: 2.462(2)	–	[252]
$[Li(THF)][(TMTAA)_2Ce]$	2.450(6)–2.502(5)	1.53	[253a]
	2.649(7)–2.691(6)	1.83	[253b]
$[K(THF)_3]_2[(TMTAT)_2Sm_2]$	2.301(6)–2.370(6)	1.23	

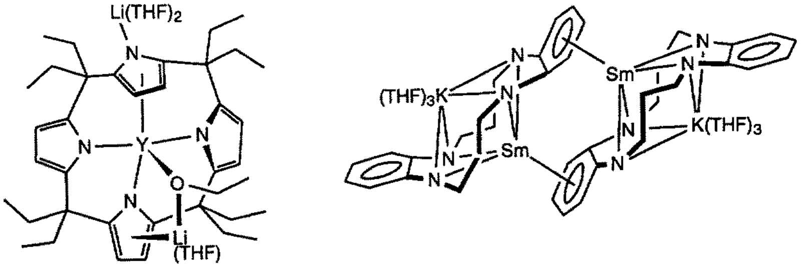


Fig. 26. Molecular drawing of $[Li(THF)_2(OEPG)Y(\mu\text{-}OEt)Li(THF)]$ and $[K(THF)_3]_2[(TMTAT)_2Sm_2]$

decane). The imide sites of the original macrocycle have been converted into amido sites which is confirmed by shorter Sm–N bond lengths relative to the abovementioned Ce-complex. Samarium is not part of the usual sandwich linkage involving 8-fold N-coordination. Here the lanthanide metal is sandwiched by one tetraamido ligand and a phenyl group of another tetraamido ligand (Fig. 26). The Sm···C contacts lie in the range 2.867(7)–3.085(7) Å.

7 Applications

7.1 Synthesis

7.1.1 The Silylamide Route

The resurgence of organometallic lanthanide amide chemistry and in particular that of the silylamides is certainly connected with their use as key synthetic-precursors. The so-called "silylamide route" is standard procedure in synthetic lanthanide chemistry. Suitable substrates are generally more Broensted acidic compounds like alcohols, phenols, cyclopentadienyls, acetylenes, phosphanes, thiols as listed in Scheme 12 [133, 140, 254–263].

$$\mathrm{Ln{-}N(SiMe_3)_2 + HL \rightarrow Ln{-}L + HN(SiMe_3)_2}$$

HL=	H–C≡CR	[254]	$\mathrm{H{-}NR_2}$	[93]	H–OR	[257]	H–Cl [263]
	H–Cp	[255]	$\mathrm{H{-}PR_2}$	[125]	H–OPh	[258]	
	H–SnR	[256]			$\mathrm{H{-}OSiR_3}$	[259]	
					H–SR	[261]	
					H–SeR	[262]	
					H–TeR	[262]	

Scheme 12. The silylamide route

The synthesis of pure precursor molecules is crucial, e.g., $\mathrm{Ln(OR)_3}$ or $\mathrm{Ln(SeR)_2}$. Well-defined compounds which contain specific element compositions are attractive for ceramic and electronic materials or catalysts in organic transformations. Hitchcock et al. reported the synthesis of monomeric homoleptic lanthanide(III) aryloxides according to this route for the first time in 1983 [258].

In particular the redox stability of lanthanide cations makes the route superior to, e.g., the usual metathesis reaction involving lanthanide halides. The advantages are evident:

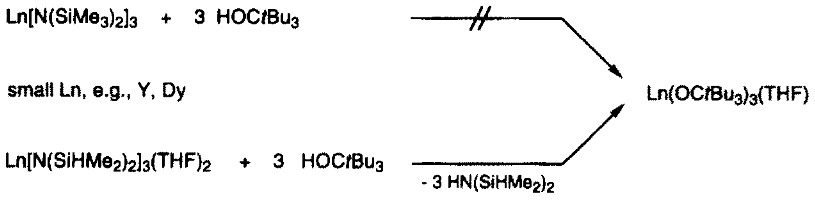
(i) facile availability of mono- and heterobimetallic amides;
(ii) reaction in noncoordinating solvents because of the high solubility of the monomeric metal amides (no adduct formation);
(iii) mild reaction conditions;
(iv) avoidance of halide contamination;
(v) easy purification of the products (removal of the released amine along with the solvent under vacuum (b.p. $\mathrm{HN(SiMe_3)_2}$: 125 °C);
(vi) donor-ligand free products (steric requirements of the released amine discourage subsequent metal coordination);
(vii) "quantitative yield".

A limiting factor of this specific btsa route is the steric bulk of the btsa ligand. Hence the exchange reaction with other bulky ligands such as Cp*H, tritox-H or phosphanes can be totally suppressed or is incomplete as in, e.g., $\mathrm{KSmCp^{*}_{2}[N(SiMe_3)_2]}$ [148].

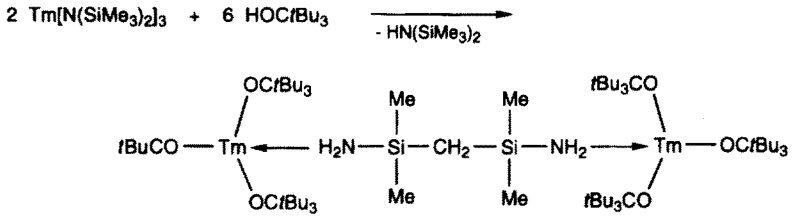
The influence of steric factors was thoroughly studied in the reaction of $\mathrm{Ln(btsa)_3}$ with the alcohol tritox-H. While the reaction takes place with larger lanthanides like neodymium to yield the homoleptic alkoxide complexes (Eq. 18) [264], the analogous reaction does not work with smaller metals like yttrium and thulium (Eq. 19). However, variation of the reaction conditions to a stoichiometric solid reaction yielded a fully exchanged product along with an unexpected and unusual silylamine degradation [265] (Eq. 20). This degradation reaction seems to be sterically forced and points out N–Si bond disruptions and C–Si bond formations under mild conditions [114].

$$\text{Ln[N(SiMe}_3)_2]_3 + 3\ \text{HOC}t\text{Bu}_3 \xrightarrow[-3\ \text{HN(SiMe}_3)_2]{} \text{Ln(OC}t\text{Bu}_3)_3 \qquad (18)$$

large Ln, e.g., Nd



(19)



(20)

Similar ligand fragmentations have been observed by reactions of Ln(btsa)$_3$ with excess alcohol component in solution. Though the reaction of Sc(btsa)$_3$ with three equivalents of silox-H resulted in a complex mixture due to degradation of the amides, Sc(silox)$_3$(NH$_3$) could be isolated from the 5-equivalent reaction (Eq. 21) [266]. In reactions with excess fluorinated alcohols HOR^F the bulkiness of the alkoxide ligand and the electronegativity of the CF$_3$ groups effect the ammoniate formation (Eq. 22) [267]. The production of the ammoniate is also suppressed by conducting the reaction in ether solvents.

$$\text{Sc[N(SiMe}_3)_2]_3 + 5\text{HOSi}t\text{Bu}_3 \xrightarrow[-2\text{HN(SiMe}_3)_2]{} \text{Sc(OSi}t\text{Bu}_3)_3(\text{NH}_3) + 2\text{Me}_3\text{SiOSi}t\text{Bu}_3 \qquad (21)$$

$$\text{Ln[N(SiMe}_3)_2]_3 + \text{excess HOR}^F \xrightarrow[-2\text{HN(SiMe}_3)_2]{} [\text{Ln(OR}^F)_3(\text{NH}_3)] + 2\text{Me}_3\text{SiOR}^F \qquad (22)$$

HOR$^F_3$	Reaction for Ln	
	+	–
HOCH(CF$_3$)$_2$	Sc, Y, Pr	
HOCMe(CF$_3$)$_2$	Y, Eu, Pr, La	Sc
HOCMe$_2$(CF$_3$)		Y, Pr

Now, back to the tritox-reaction. The reactivity-determining influence of the ligand constitution has been examined by introduction of the sterically less crowded bdsa amide ligand (Fig. 27) [114]. This ligand offers a valuable extension of the silylamide route:

(i) change in ligand basicity changes the reactivity of the lanthanide metal;
(ii) decreased steric bulk favors the attack of the protic reagent;
(iii) lower b.p.(93–95 °C) of the released amine facilitates work-up procedure

According to this extended silylamide route, completely exchanged Ln(tritox)$_3$(THF) are formed easily and in high yield for the smaller lanthanides. THF dissociation in solution probably induces the reaction of Ln(bdsa)$_3$(THF)$_2$ with tritox-H.

Corresponding reaction behavior has been observed for the sterically similar N*i*Pr$_2$ ligand. In the reaction of LiLa(N*i*Pr$_2$)$_4$ with P(C$_6$H$_4$OMe-*o*)$_2$H, two N*i*Pr$_2$ were exchanged with the secondary phosphine, while it was impossible to replace more than one N(SiMe$_3$)$_2$ ligand in Ln[N(SiMe$_3$)$_2$]$_3$ [79]. The enhanced reactivity was assigned to higher basicity and steric flexibility of the N*i*Pr$_2$ group. However, application of the N*i*Pr$_2$ ligand in synthesis is more controversial, because supply of well-defined Ln(N*i*Pr$_2$)$_3$ precursors is hampered by *ate* complexation (Sect. 3.1). Enhanced thermal instability compared to the bdsa analogues is expressed in decomposition upon attempted sublimation (100 °C/10^{-4} torr) [82].

The silylamide route is also transferable to lanthanide(II) chemistry. However, now steric effects are of minor importance due to the enhanced steric flexibility of Ln(II) amides. Eu(II) and Yb(II) silylamides are accessible to exchange reactions for all reagents listed in Scheme 6. For example

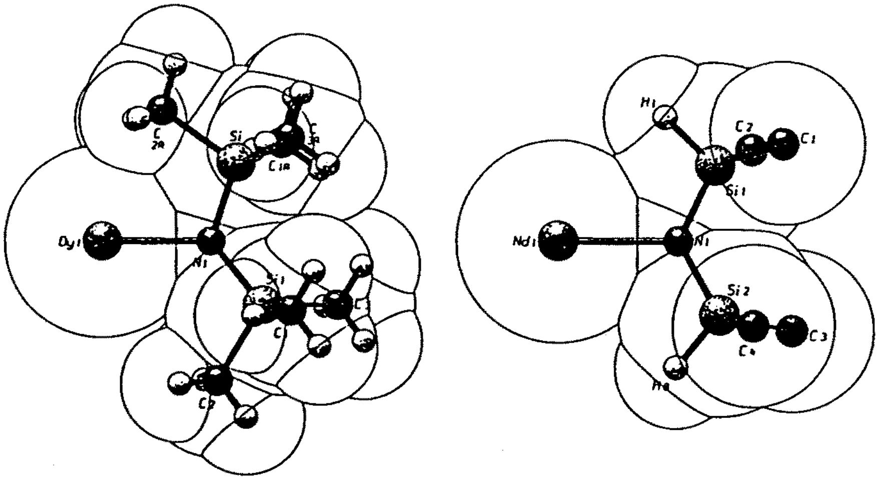


Fig. 27. Steric shielding of btsa and bdsa ligands

$[Yb(tritox)_2]_2$ is readily formed [150]. The strongly reducing and thermally unstable Sm(II) amides tend to get oxidized by alcohols under the usual conditions [268]. However, aryloxides have been isolated, especially when they are stabilized by *ate* complexation as in the case of $[KSm(OC_6H_3\text{-}2,6\text{-}t\mathrm{Bu}_2)_3(THF)]_n$ [269]. In addition, the latter complex represents another approach of the silylamide route, namely the generation of mixed metallic complexes by retention of the original metal composition of the amide.

Recently solutions of europium and ytterbium in liquid ammonia have been rediscovered as a precursor system to highly pure exchanged complexes [270]. The active species in these reactions are the hexaammoniates and the only byproducts are hydrogen and ammonia (Eq. 23a–c).

$$Eu + mNH_{3\mathrm{liq}} \rightarrow Eu^{2+}(NH_3)_6 \cdot 2e^-(NH_3)_n \tag{23a}$$

$$2HR + 2e^-(NH_3)_n \rightarrow 2R^- + H_2 + nNH_3 \tag{23b}$$

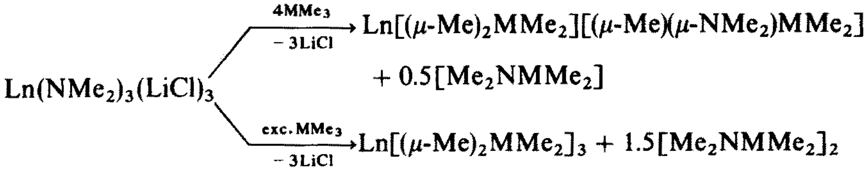
$$Eu^{2+}(NH_3)_6 + 2R^- \rightarrow EuR_2 + 6NH_3 \tag{23c}$$

According to this procedure, compounds like $EuCp_2$ [271, 272], $YbCp^*_2(NH_3)_x$ [69], Ln(COT) (Ln = Eu, Yb) [273, 274], $Eu(CH_3{\equiv}C)_2$ [275], $Eu(PH_2)_2$ [276], $Yb(OC_6H_2t\mathrm{Bu}_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3$ [261], LnX_2 (Ln = Eu, Yb; X = Cl, Br, I) [277] have been synthesized. The reactivity of europium in liquid ammonia with organosulfur and organophosphorus acids as well as with d,l-α-alanine was also investigated [278]. More recently complexes of divalent lanthanides with decaborates, e.g., $(NH_3)_xYb(B_{10}H_{14})$ have been reported [279].

Heterogeneous reactions of lanthanide metals dissolved in liquid ammonia with free hydroxy groups of silica, alumina or zeolites yielded supported lanthanide species which display various catalytic activity (Sect. 7.2). In complexes of type $Eu(bipy)_4$, $Yb(o\text{-}phen)_4$ the dipositive cation is assumed to be coordinated by radical anion-like ligands [280]. Ammonia may also act as an alternative medium for the synthesis of homoleptic lanthanide(III) complexes.

7.1.2 Alkylation Reactions

Lanthanide alkyls are not available according to the silylamide route and were obtained by another synthetic approach [60]. The Lewis basic N(amide) atom induces this bond transformation via interaction with strong Lewis acidic alkyls. By this course heterobimetallic addition complexes involving group(IIIB) metal alkyls and amide ligands NMe_2, $N\mathit{i}Pr_2$, $N(SiMe_3)_2$ and NHPh could be isolated as initial products (Sect. 3.1). The prospitious ligand and metal constellation enables stepwise exchange of amide through alkyl ligands (Scheme 13). The resulting peralkylated mixed metallic complexes are stable at room temperature [60]. The formation of a strong group(IIIB) metal-N(amide) bond may drive the reaction to completion.



$$\mathrm{Ln(NMe_2)_3(LiCl)_3} \xrightarrow[-3\mathrm{LiCl}]{4\mathrm{MMe_3}} \mathrm{Ln[(\mu\text{-}Me)_2MMe_2][(\mu\text{-}Me)(\mu\text{-}NMe_2)MMe_2]_2} + 0.5\mathrm{[Me_2NMMe_2]}$$

$$\mathrm{Ln(NMe_2)_3(LiCl)_3} \xrightarrow[-3\mathrm{LiCl}]{\mathrm{exc.\,MMe_3}} \mathrm{Ln[(\mu\text{-}Me)_2MMe_2]_3} + 1.5\mathrm{[Me_2NMMe_2]_2}$$

Scheme 13. Alkylation of lanthanide amides (M = Al, Ga)

Again the reactivity is determined by steric factors. For example, $\mathrm{La(btsa)_3}$ does not show any tendency to react with group(IIIB) metal alkyls under these conditions [89]. However, total ligand exchange has been proven in $\mathrm{Sm(btsa)_2(THF)_2}$ and $\mathrm{KSm(btsa)_3}$ by NMR- and IR-spectroscopy to yield the first Sm(II) alkyls [89].

As part of these studies a rare one pot reaction sequence consisting of three different steps (adduct formation, ligand exchange and CH_4 elimination) has been observed (Eq. 24) [93]. The molecular structure of the resulting complex is shown in Fig. 28.

$$\mathrm{Nd(NHPh)_3(KCl)_3} \xrightarrow[-3\mathrm{KCl}]{6\mathrm{AlMe_3}} \mathrm{\{Nd[(\mu\text{-}Me)_2AlMe_2]_2\}_2[(\mu\text{-}NPh)AlMe(\mu\text{-}Me)]_2} + 2/3\mathrm{[Me_2AlNHPh]_3} + 2\mathrm{CH_4} \qquad (24)$$

Furthermore the homoleptic Ln-anilides might open up a similar route to lanthanide alkyls as do lanthanide phenoxides [281].

7.2 Materials

Chemical vapor deposition of nitride films from homoleptic early transition metal and main group amide single source precursors is well documented [282]. Homoleptic $\mathrm{Ln(btsa)_3}$ complexes belong to the most volatile lanthanide compounds. They almost approach the volatility of cyclopentadienyl complexes like $\mathrm{Ln}(t\mathrm{BuCp})_3$ which are especially designed for this purpose [283, 284]. The thermogravimetric examination of both classes of compounds show the typical weight loss for volatile compounds during the phase of dynamic heating (Fig. 29).

Cyclopentadienyl compounds have been thoroughly investigated as suitable precursors to rare earth doped semiconductors in MOCVD (metal-organic chemical vapor deposition) or MOVPE (metal-organic vapor phase epitaxy) processes [283]. The use of btsa complexes for the same purpose has appeared in the literature very recently [285]. Typical process conditions are shown in Scheme 14. It was found that the carbon contamination of the deposited metal is less in the btsa case.

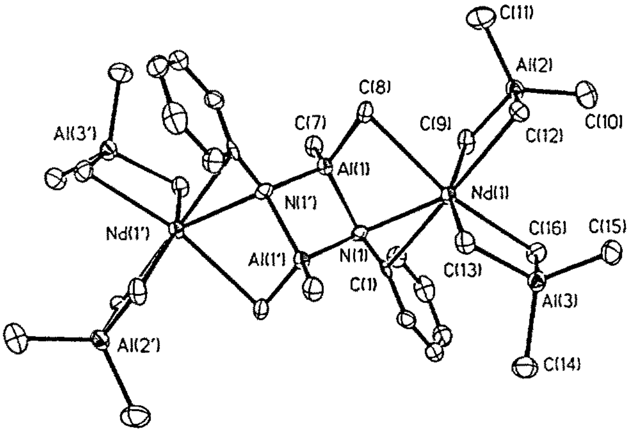
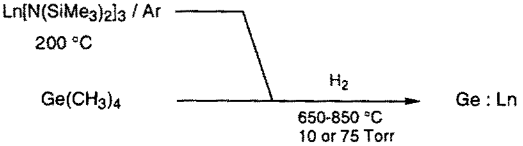


Fig. 28. Molecular structure of $\{Nd[(\mu\text{-}Me)_2AlMe_2]_2\}_2[(\mu\text{-}NPh)AlMe(\mu\text{-}Me)]_2$ [93]



Scheme 14. Use of $Ln(btsa)_3$ in doping of semiconductors

$$Ln[N(SiMe_3)_2]_3 + x \xrightarrow[150-180\,^\circ C]{N_2(g)} \text{Melt} \xrightarrow[210\,^\circ C]{NH_3(g)} \xrightarrow[500-800\,^\circ C]{\text{Annealing}} LnN_{1-x}$$

x = e.g., $LiN(SiMe_3)_2$

Scheme 15. Silylamides as precursors to nitrides

Low temperature processes are desirable in material sciences. Lanthanide nitrides which possess intrinsic electronic and magnetic properties are typically synthesized by ammonolysis of the metals at temperatures near 1000 °C. Inorganic amides of type $Ln(NH_2)_x (x = 2, 3)$ are intermediates in this process (Sect. 2.1). A versatile method starting from molten $Ln(btsa)_3$ precursors was reported by LaDuca and Wolczanski [286]. The formation of low crystalline LnN_{1-x} according to Scheme 15 was observed at about 210 °C after 3 h.

Crystalline LnN_{1-x} [$x \leq 0.1$(Nd) and $x \leq 0.2$(Sm)] were obtained by annealing under NH_3 up to 850 °C. Impurities of LiCl or $LiNH_2$ lowered the annealing temperature to 475 °C due to mineralization processes.

Lanthanide(III) Pc doubledecker complexes, $LnPc_2$, possess peculiar electronic properties which make them the first molecular semiconductors [287]. Applications in the field of high speed thin film electronics have been discussed (by Simon et al.). Like the silylamides, they are also sublimable. The radical

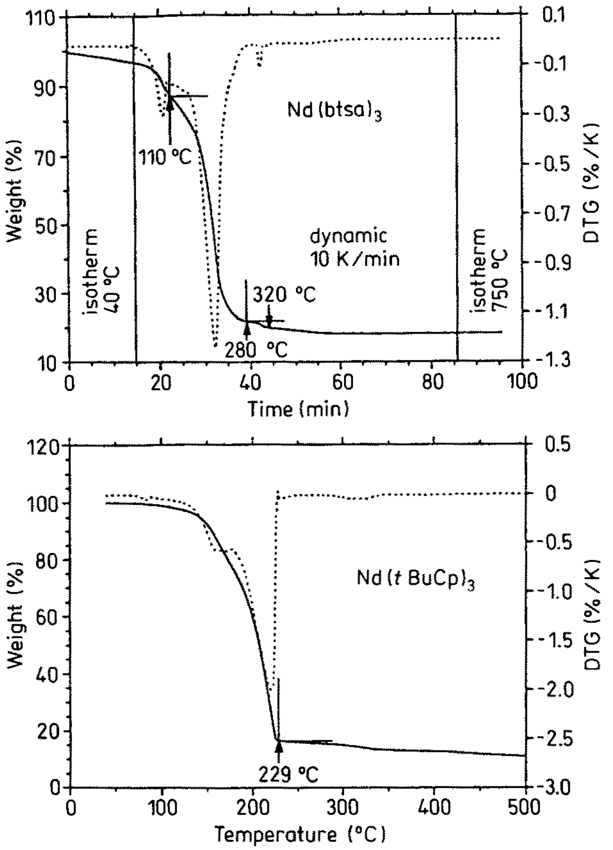


Fig. 29. TG-DTG curves of: Nd(btsa)$_3$ (*top*) and Nd(*t*BuCp)$_3$ (*bottom*) [284]. The coupled mass spectra revealed btsa-CH$_3$ and *t*BuCp-CH$_3$ as base peaks

nature of the electroneutral molecules has been shown by the presence of one spin-1/2 per LuPc$_2$ molecule in the ESR spectra [287]. LnPc$_2$ are easily reduced and oxidized (Eq. 25) which correlates with a small activation energy of conduction of 0.52 eV for lutetium.

$$\mathrm{Pc_2Lu^+} \underset{+0.03}{\rightleftharpoons} \mathrm{Pc_2Lu} \underset{-0.45}{\rightleftharpoons} \mathrm{Pc_2Lu^-}$$

$$\Delta E = E^{ox}_{1/2} - E^{red}_{1/2} = 0.48\,\mathrm{V} \tag{25}$$

Both single crystals ($6 \times 10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$) and sublimed thin films ($10^{-5}\,\Omega^{-1}\mathrm{cm}^{-1}$/high vacuum) of LuPc$_2$ show room temperature conductivity which are more than six orders of magnitude higher than for MPc derived from divalent Cu, Ni and Zn.

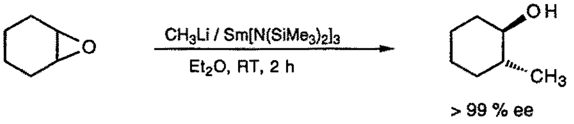
Aiming at doped liquid crystalline conductors, the electrochromic and conducting properties of the Lu-Pc system were tested in columnar liquid crystals [288]. The mesophase of long alkoxy chain derivatives, e.g., $[(C_{12}H_{25}O)_8Pc]_2Lu$ and $[(C_{12}H_{25}O)_8Pc]_2Lu^+BF_4^-$ exist in ordered hexagonal structures in temperature ranges of 85–189 °C and –3 to 253 °C, respectively. The macroscopic conductivities of these discogens are extremely low $(<10^{-10} - 10^{-12}\,\Omega^{-1}cm^{-1})$.

More recently crownether substituted $LuPc'_2$ has been introduced into iono-electronics [289].

7.3 Catalysis

Organic transformations mediated by stoichiometric or excess amounts of lanthanide agent shall be discussed first in this section.

Mukerji et al. has reported the regioselective alkylation of epoxides with the *ate* reagent $MeLi/Ln(btsa)_3$ (Eq. 26) [290]. The stereoselectivity of the alkylation reaction of styrene oxide and butadienoxide is complementary to that of organocopper reagents.



(26)

Homogenous desulfurization of thiols and sulfides can be achieved by stoichiometric use of $Yb(btsa)_2(THF)_2$ as expressed in Eq. (27) [291]. The desulfurization reaction is assumed to proceed via one electron reduction of the substrate and its extent to be dependent on the stability of the radical intermediates.

$$Yb[N(SiMe_3)_2]_2 + HSR \rightarrow [N(SiMe_3)_2]Yb{-}SR + HN(SiMe_3)_2$$

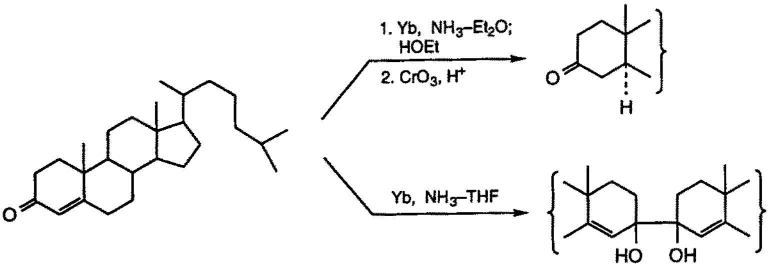
$$[N(SiMe_3)_2]Yb{-}SR \rightarrow R^{\cdot} + \{[N(SiMe_3)_2]Yb{-}S\}^{\cdot} \rightarrow \{[N(SiMe_3)_2Yb^{III}{-}S{-}\}_n \tag{27}$$

Carbon dioxide fixation by $Ln(btsa)_3$ (Ln = Nd, Pr) has been reported [292].

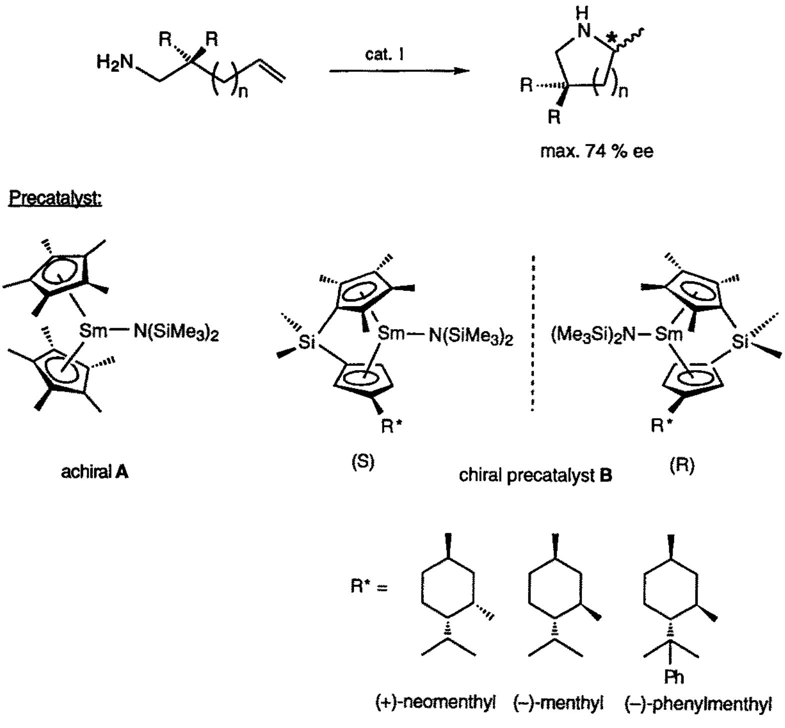
Solutions of ytterbium in liquid ammonia are capable of reducing aromatic systems to 1,4-dihydroaromatics or alkynes to trans alkenes [293]. The α,β-unsaturated cholest-4-en-3-one was reduced to cholestanone in 80% yield by threefold excess of ytterbium in ammonia followed by oxidation with Jones' reagent (Scheme 16). In the absence of a proton source, (HOEt) and THF as co-solvent, the pinacol dimer was obtained as the major product.

7.3.1 Homogeneous Catalysis

Most extensively, as well as most impressively, studied is the organolanthanide-catalyzed hydroamination/cyclization of N-unprotected aminoolefins by



Scheme 16. Solutions of ytterbium in ammonia as synthetic agents



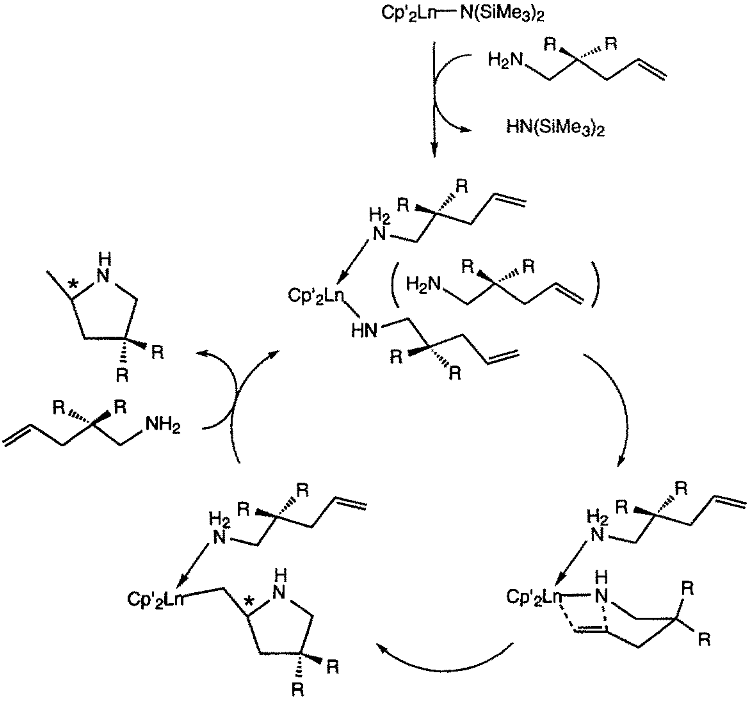
Scheme 17. Organolanthanide-catalyzed hydroamination/cyclization of N-unprotected aminoolefins

Marks et al. [77, 294]. The formation of heterocyclic nitrogen compounds is of relevance in natural products, particularly in alkaloid synthesis, when the formation of the C–N bond occurs with asymmetric induction. The cyclization is not restricted to primary amines and produces 2-methylheterocycles (5-, 6-, 7-membered) with >99% regioselectivity and a new asymmetric center adjacent to the heterocyclic nitrogen atom (Scheme 17).

Achiral precatalysts of type **A** form racemic products. However, high enantioselectivity is obtained by C1-symmetric chiral precatalysts **B**. The turnover frequencies N_t are dependent on the type of substrate and correlate with the coordinative unsaturation at the metal center. That means N_t is higher for larger elements and increases in order of, e.g., following ligand composition: $Cp^*_2Lu[CH(SiMe_3)_2]$ (< 1 h^{-1}) < $[MeSi(CpMe_4)_2]Lu[CH(SiMe_3)_2]$ (75 h^{-1}) < $[Et_2Si(CpMe_4)Cp]Lu[CH(SiMe_3)_2]$ (200 h^{-1}) [77]. N_t of chiral precatalysts (max. 93 h^{-1}) are about 10 times those of the Cp^*_2Lu-catalyzed reaction, obviously reflecting the steric situation. N_t are indistinguishable for H-, $CH(SiMe_3)_2$-and $N(SiMe_3)_2$-type precatalysts, which favors the more easily synthesized amide derivative.

The overall high enantioselectivities are increased at lower temperature and can attain up to 74% ee. Epimerization is observed during the initiating rapid protonolysis reaction, but the optical purity of the precatalyst does not influence the configuration and optical purity of the product.

Kinetics and mechanism (Scheme 18) of the reaction have been thoroughly investigated by means of in situ ^1H NMR and isotopic labelling. The studies suggest essentially zero order dependence on the substrate concentration, but, also point out a competitive inhibitor functioning of the product heterocycles. Rapidly formed amine-amide adducts of type $Cp_2Ln(HNR)(H_2NR)$ are assumed to be the active catalyst [77]. The turnover limiting process is the



Scheme 18. Mechanism scheme for organolanthanide-catalyzed hydroamination

intramolecular olefin insertion into the Ln–N bond which proceeds via a chair-like, 7-membered transition state.

As expected, the chiral precatalysts also initiate diastereoselective processes ($>95\%$) [294c].

The same type of precatalysts catalyze the regiospecific hydroamination/cyclization of aliphatic and aromatic aminoalkynes $RC\equiv(CH_2)_nNH_2$ [295]. The mechanistic scenario parallels that of the corresponding aminoolefin cyclization. However, the cyclization of the aminoalkynes is 10–100 times more rapid, and a rather contrary effect of the cyclopentadienyl substitution on N_t was observed.

The catalytic potential of the above mentioned "Cp_2LnR"-type precatalysts was first recognized in olefin polymerization reactions [296] and the hydride derivatives ($R=H$) represent excellent single component catalysts for the oligomerization of ethylene (e.g. $>1800\,s^{-1}$, 1 atm ethylene, 25 °C) [297]. However, propylene oligomerization is limited by chain lengths $C < 24$ (C = number of carbon atoms). The scandium complex $\{[Cp^*Me_2Si(\eta^1\text{-}NtBu)]Sc(PMe_3)\}_2(\mu\text{-}H)$ containing a linked cyclopentadienyl-amide ligand is also capable of oligomerization of the α-olefins propene, 1-butene and 1-pentene [164]. Chain propagation occurs rather slowly (pentene: 52 turnovers/(Sc/h)) with $>99\%$ "head to tail" coupling to afford linear atactic polymers with a number of average molecular weights of 3000–4000 and a polydispersity index (PDI) of 1.7–2.1. Participation of all Sc-centers in the polymerization was evidenced by the molecular weight distribution of the oligomers at low propene conversion. Complexes $\{[Cp^*Me_2Si(\eta^1\text{-}NtBu)]Sc(PMe_3)\}_2(\mu,\eta^2,\eta^2\text{-}C_2H_4)$ and $\{[Cp^*Me_2Si(\eta^1\text{-}NtBu)]Sc\}_2(\mu\text{-}CH_2CH_2CH_3)_2$ could be obtained from stoichiometric reactions of $\{[Cp^*Me_2Si(\eta^1\text{-}NtBu)]Sc(PMe_3)\}_2(\mu\text{-}H)_2$ with two equivalents of ethylene and propene, respectively.

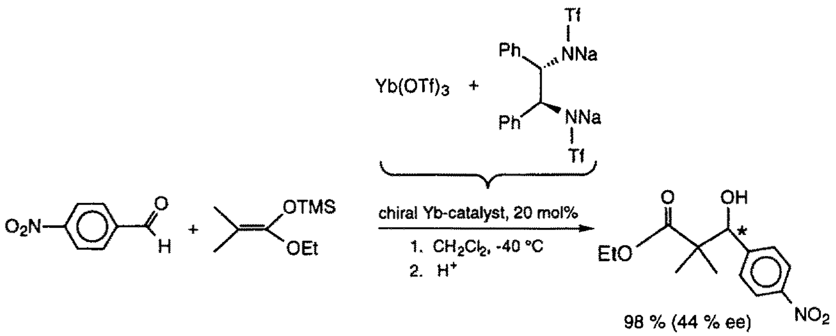
Sm(II) amides display extraordinary reactivity in catalytic caprolactone polymerization [298]. Among other complexes $Yb(btsa)_2(AlEt_3)_2$ and $Y(C_3H_5)_2[N(SiMe_2CH_2PMe_2)_2]$ exhibit catalytic activity in ethylene oligomerization [144, 169].

Asymmetric lanthanide complexes derived from lanthanide triflates and a chiral bidentate sulfonamide ligand were applied to the Mukaiyama aldol reaction (Scheme 19) [299]. Enantiomeric excesses were moderate and the reaction proceeded best in CH_2Cl_2 solvent and with ytterbium as metal center.

7.3.2 Heterogeneous Catalysis

Immobilization of lanthanide species in catalytically active form was achieved by contacting solutions of lanthanide metals (Eu, Yb) in liquid ammonia with oxide, metal powders and active carbon "AC" (Imamura et al., Ono et al. [300–310] Scheme 20). Extent of lanthanide loading and evacuation temperatures of the hybrid catalyst markedly affect the catalytic behavior.

FT-IR studies indicate that the lanthanide species supported on oxidic materials can be assigned to an amide structure according to Eq. (28) [300, 301].



Scheme 19. Mukaiyama aldol reaction mediated by asymmetric sulfonamide complexes

SiO_2[300, 301] Al_2O_3 [302] MgO, MnO, Fe_3O_4 [300]	Ni–SiO_2 [303] Pd–SiO_2 [304]	Fe [305], Ni [306, 307], Co [308], Cu, Ag [306, 309]	AC [310]
hydrogenation, *disproportionation*	*hydrogenation*	*dehydrogenation/hydrogenation* *hydrogenolysis*	*cyclization*
M^{I}Y-zeolite [305] *hydrogenation, isomerization* *Michael reaction*			

Scheme 20. Supports used for immobilization of Eu and Yb species – catalytic activity

The hybridic systems exhibit selective hydrogenation of conjugated and non-conjugated double bonds. Polyvinyl alcohol, PVA, and $HOSiPh_3$ were used as model compounds [301].

$$\equiv \text{Si–OH} + \text{Ln}^{2+}(\text{NH}_3)_6 \cdot 2e^-(\text{NH}_3)_n \rightarrow \equiv \text{Si–O–Ln–NH}_2 + \text{H}_2 + (n + 5)\text{NH}_3 \qquad (28)$$

Catalytic activity in zeolitic materials is strongly influenced by the type of alkali metal cations, and maximum catalytic activity, e.g., in isomerization reactions, is explained by the formation of an imide species "EuNH" [305]. Synergetic effects were observed in bimetallic supported SiO_2 which showed considerable hydrogen uptake during hydrogenation reactions [307]. The formation of Ln–NH_2, -NH, -N species seemed to be suppressed in the presence of transition metal powders and precipitation of elemental lanthanides is favored [309]. Lanthanide imides were favored as active species in the Ln/AC-mediated cyclization of ethyne and propyne [310].

7.4 Medicine

Today, the application of lanthanide elements in clinical medicine focusses on their diagnostic properties, with emphasis on spectroscopic probes [311]. The nuclear characteristics of ^{165}Dy, ^{166}Ho and ^{169}Er have been examined in radiotherapy (synoviotherapy) [312]. In the course of these studies two contrary investigations have to be taken into consideration. Due to similar features in coordination chemistry, the interaction of lanthanide cations Ln^{3+} with biological ligands like amino acids help to indicate the role of similar Ca^{2+}. As a result the investigation of the bonding mode of Ln^{3+} towards biological ligands and hence crystallographic data increased recently [313]. On the other hand, in vivo use of lanthanide complexes as spectroscopic tools requires avoidance of exactly these interactions, e.g., replacement of the essential Ca^{2+}. Considering this, the administered complexes have to be very stable. As a consequence numerous polyanionic and macrocyclic ligands have been introduced as carrier of the "lanthanide satellites". Recently, amide derived complexes became involved.

7.4.1 Magnetic Resonance Imaging (MRI)

Gadolinium(III) derived complexes are potentially one of the best contrast agents in ^{1}H NMR imaging [314]. Long electron spin correlation times ($t > 10^{-10}$) (dipolar interactions) of Gd(III) decrease the relaxation times and thus increase the image intensity of nearby nuclei, largely composed of water protons [315]. At present, three carboxylate-based complex Gd(III)-derived MRI contrast agents have been approved for human clinical use in the United States, namely the bis-*N*-methylglucamine salt of Gd(III) diethylenetriaminepentaacetic acid (DTPA) (Magnevist), the bis-*N*-methylamide of Gd(III)(DTPA) (Omniscan), and the Gd(III) chelate of the 10-(2-hydroxypropyl) derivative of 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-1,4,7-triacetic acid (Prohance) [246c, 314]. To better match the stringent biological requirements such as relaxivity, target-specific in vivo distribution, in vivo stability, water solubility, excretability, and lack of toxicity, new ligand environments are currently being tested. One approach is the introduction of water soluble porphyrin complexes like TPPS [316,317]. "Expanded porphyrins" are reported to be kinetically even more stable (Sect. 6.3.3) and first in vivo experiments support the fact that LnTx complexes are promising candidates for the imaging of kidney, liver and neoplastic tissues [318].

Dy(III) complexes have been found to be particularly effective shift agents in ^{23}Na NMR imaging [319]. When placed in polyanionic ligand environments which can bind cations like sodium, Dy(III) can induce large hyperfine shifts within their neighbors. Thus it is possible to distinguish intra- and extracellular sodium cations [320]. Chelate ligands applied so far, e.g., polyphosphates, suffer from problems as metal dissociation and therefore competitive binding of other biologically significant cations occur [321]. Facing this problem, Tx ligands

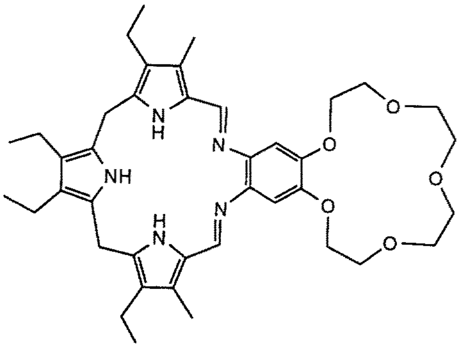


Fig. 30. Modified Tx ligands which can accommodate different cations

have been modified to provide additional binding sites specifically for alkali metals [322]. It has been shown by determination of hyperfine ^{23}Na NMR shifts that crown ether fused systems (Fig. 30) are capable of binding lanthanides as well as sodium cations [323].

7.4.2 Catalytic Cleavage of RNA

The functionalization of LnTx complexes can be directed in various ways. An EuTx bearing activated estergroups can react with oligodeoxynucleotide amine to form DNA-EuTx conjugates. The resulting "ribozyme analogue" shows site-specific hydrolysis of RNA [323]. The chromophoric properties of LnTx were used to achieve oligonucleotide-directed, sequence-specific photocleavage of DNA with irradiation above 700 nm [324a]. Because of exactly these photophysical properties and the observation that porphyrin-like moieties can localize and/or are retained selectively in rapidly growing tissues, LnTx are also discussed in photodynamic therapy (PDT) [246c, 324b].

8 Conclusion and Perspective

Is there a small cluster chemistry based on lanthanide amides? Is alkali metal *ate* complexation just an annoying fact? Is there a real potential for lanthanide amides in material sciences and catalysis? The synthetic chemist is challenged by these questions and more, and hopefully the previous sections can deliver some basic tools for tackling these topics.

The use of lanthanide amides in synthetic chemistry is meanwhile established and fine tuning of the ligands provides new targets. Examination of small ligands started recently and their exploration as precursors to, e.g., moisture stable, ternary nitrides might be promising. However, the search for low coordinated, highly reactive lanthanide centers will continue to involve new bulky amide ligands [325]. They will, together with the steadily growing number of tailor-made, multiply chelating macrocycles, offer a welcome alternative to the ubiquitous cyclopentadienyl ligand. Intriguing coordination chemistry was already indicated by porphyrinogen derivatives [67, 251].

Amines and "N–C" moieties are fundamental building blocks in organic chemistry and lanthanide elements with their unique properties [326] recently became involved in this cycle. The pioneering work of Marks [77, 294] in lanthanide amide catalyzed formation of C–N bonds is encouraging. Future introduction of other chiral co-ligands as binols [327, 328] or even asymmetric amide ligands themselves are likely. Functionalized amide ligands [329], whose powerful ligation mode has been proven, seem to be especially suitable considering the reservoir of chiral lithium precursors [330]. The stabilizing effect of amide ligands on the more unusual and more reactive oxidation states Sm(II) and Ce(IV) may also contribute to the perspectives in catalysis.

Supposedly, lanthanide chemistry is lagging behind main group and d-transition metal chemistry. The concluding statement which Bradley made with respect to transition metal dialkylamides and silylamides almost 20 years ago [19b] is a current topic in lanthanide amide chemistry: "To date homogenous transition-metal catalysis has been restricted to hydrocarbon systems involving the facile formation and rupture of M–H, M–C, C–H and C–C bonds. An extension to include M–N, C–N, M–O, and C–O bonds seems plausible and could lead to substantial advances in transition-metal catalysis."

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Rare Earth Complexes with Heteroallylic Ligands

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Table of Contents

The chemistry of rare earth complexes containing bulky heteroallylic ligands is reviewed. Sterically demanding heteroallylic ligands are shown to be very promising alternatives for cyclopentadienyl ligands in lanthanide chemistry. In particular, the easily accessible *N*-silylated benzamidinate ligands $[RC_6H_4C(NSiMe_3)_2]^-$ may soon rival $C_5H_5^-$ and $C_5Me_5^-$ in their high versatility. Heteroallylic ligands are capable of stabilizing reactive lanthanide(II) complexes (e.g. $[RC_6H_4C(NSiMe_3)_2]_2Yb(THF)_2$ **12o**) as well as homoleptic complexes of the type $[RC_6H_4C(NSiMe_3)_2]_3Ln$ (**20–23**), the latter being useful precursors for lanthanide-based materials (Ln_2O_3, Ln_2S_3, Ln_2Se_3). Of special interest for future applications are functionalizable bis(ligand) lanthanide halides and triflates (e.g. $[RC_6H_4C(NSiMe_3)_2]_2YCl(THF)$ (**35b**) and $[Ph_2P(NSiMe_3)_2]_2LnCl(THF)$ (**56**)) and the σ-alkyl and hydride derivatives thereof. Implications for the development of novel homogeneous catalysts are discussed.

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1 Introduction

Due to the numerous industrial applications of the rare earth elements and their compounds [1–3], modern lanthanide chemistry is an area of vigorous research. This is especially true for organolanthanide chemistry [4–8], which has produced an impressive number of highly active homogeneous catalysts [9, 10]. Various olefin and alkyne transformations are effectively catalyzed by organolanthanide complexes [8–11]. Typically the most active catalysts are compounds of the type $(C_5Me_5)_2LnX$, where X is a hydride ligand or a hydrocarbyl ligand such as methyl or bis(trimethylsilyl)methyl [12–18]. The organolanthanide hydrides are usually dimerized through bridging hydride ligands.

Surprisingly little is known about catalytically active lanthanide complexes containing other ancillary ligands than $C_5H_5^-$ or $C_5Me_5^-$ [19–21]. In fact, an estimated 90% of all organolanthanide complexes contain supporting ligands of the cyclopentadienyl type [8]. Therefore substantial research activities are currently directed towards the development of alternative ligand systems which eventually may rival the cyclopentadienyl ligands in their high versatility [22, 23].

Table 1 shows the assignment of the various lanthanide elements in the numbering of the compounds in this article. As usual, scandium and yttrium have been included because of their chemical similarity with the lanthanides. Not included was the radioactive promethium for which no complex containing heteroallylic ligands has so far been reported.

2 Results and Discussion

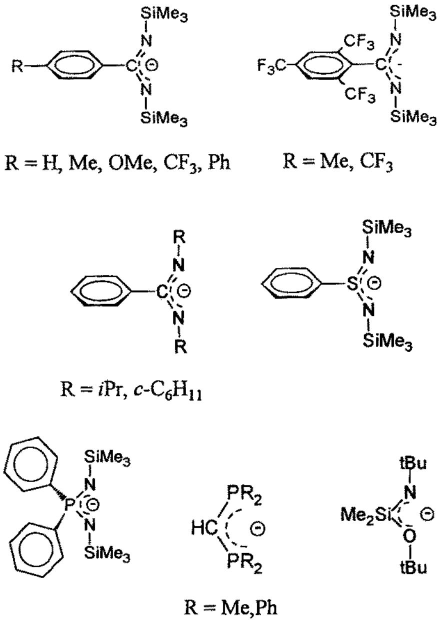
One of the most successful approaches towards alternative ligand sets for lanthanide complexes is the use of bulky heteroallylic ligands. These ligands have been shown to behave as “steric cyclopentadienyl equivalents” [24], i.e. their cone angle is very similar to that of $C_5H_5^-$ or $C_5Me_5^-$. Scheme 1 shows the heteroallylic anions which have been successfully employed.

These anionic ligands, especially those containing trimethylsilyl substituents [25, 26], combine several unique features which make them extremely useful for lanthanide chemistry.

1. The cone angle of $[RC_6H_4C(NSiMe_3)_2]^-$ and $[PhS(NSiMe_3)_2]^-$ is roughly comparable with that of $C_5H_5^-$ or monosubstituted cyclopentadienyl ligands. On the other hand the chemistry of $C_5Me_5^-$ can be matched by using the very bulky ligands $[(CF_3)_3C_6H_2C(NSiMe_3)_2]^-$ and $[Ph_2P(NSiMe_3)_2]^-$. Of course these considerations are purely qualitative in nature, as the observed effects may differ to some degree depending on the ionic radii of the lanthanide elements. In the case of smaller lanthanide ions

Table 1. Numbering scheme of the lanthanide elements in this review

Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p



Scheme 1. Bulky Heterollylic Ligands

such as Y^{3+}, Yb^{3+}, or Lu^{3+} the chemistry of $[RC_6H_4C(NSiMe_3)_2]_2Ln$ derivatives more closely resembles that of $(C_5Me_5)_2Ln$ complexes than that of $(C_5H_5)_2Ln$ derivatives [27].

2. Sterically demanding alkyl or trimethylsilyl substituents provide the necessary steric saturation around the large lanthanide ions and assure a high solubility of the products in nonpolar organic solvents.
3. Just like cyclopentadienyl ligands, the heteroallylic ligands are kinetically more inert than halide, hydride, or alkyl ligands and thus allow facile substitution reactions at other reactive sites of the molecules.
4. All the above-mentioned heteroallylic ligands are easily accessible in large quantities through one- or two-step preparations. They can be isolated either in the form of lithium or sodium salts or as fully silylated neutral species.
5. The heteroallylic anions are ideal new observer ligands for lanthanides as most of them contain several NMR-observable nuclei (^1H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P).

2.1 Ligand Preparations

In general, synthetic procedures leading to lithium or sodium salts of heteroallylic ligands are simple and straightforward. Precursors such as $Li[PhC(NSiMe_3)_2]$ are easier to make than sodium cyclopentadienide! Typical preparations of the starting materials are outlined below with the examples of $Li[RC_6H_4C(NSiMe_3)_2]$ and $Na[RC_6H_4C(NSiMe_3)_2]$ as well as $Li[PhS(NSiMe_3)_2]$ and $Li[Me_2Si(OtBu)(NtBu)]$.

A crystalline addition product of benzonitrile and $LiN(SiMe_3)_2$, formulated as $LiN = C(C_6H_5)N(SiMe_3)_2$, was first described in 1973 by Sanger, who also reported mass spectroscopic and IR data on this material [28, 29]. Pure crystalline lithium and sodium salts of the *N*-silylated benzamidinate anions were first reported in 1990 [30]. Their synthesis was made possible through the use of highly pure starting materials (e.g. distilled $LiN(SiMe_3)_2$ [31]):

$$RC_6H_4CN + LiN(SiMe_3)_2 \xrightarrow{Et_2O} Li[RC_6H_4C(NSiMe_3)_2]. \qquad (1)$$

$$\mathbf{1},\ R = H, Me, MeO, CF_3, Me_2N, NO_2$$

With the exception of the less soluble *p*-methoxy derivative **1** (R = MeO), the lithium salts **1** can be recrystallized from hexane. Their high solubility even in aliphatic hydrocarbons can be attributed to the presence of two bulky and lipophilic $SiMe_3$ substituents. Thus the solubility of the silylated benzamidinates differs greatly from that of the corresponding lithium carboxylates. The facile formation of **1** (R = Me) is remarkable as *p*-tolunitrile is normally deprotonated at the methyl group upon treatment with strong bases such as $LiNMe_2$ or $LiN(iPr)_2$ [32]. In this sense the formation of **1** (R = Me) from *p*-tolunitrile and $LiN(SiMe_3)_2$ appears to be an exception from the "regular" reactivity pattern.

For synthetic purposes a number of sodium *N,N'*-bis(trimethylsilyl)benzamidinates **2** have been synthesized in an analogous manner by addition of $NaN(SiMe_3)_2$ to *p*-substituted benzonitrile derivatives [30, 33]:

$$RC_6H_4CN + NaN(SiMe_3)_2 \xrightarrow{Et_2O} Na[RC_6H_4C(NSiMe_3)_2]. \qquad (2)$$

$$\mathbf{2},\ R = H, Me, MeO, CF_3$$

Generally the yields are high (71–98%) and the sodium salts **2** are readily isolated as white, crystalline solids. Their solubility in hydrocarbon solvents decreases in the order $R = CF_3 > H > Ph > MeO$. The *p*-trifluoromethyl derivative can be recrystallized from hexane.

Very little is known about *N,N'*-bis(trimethylsilyl)benzamidinate derivatives of the heavier alkali metals, although the salts **3**–**5** have been prepared according to the reaction at Eq. (3) by treatment of benzonitrile with the corresponding alkali metal bis(trimethylsilyl)amides [25, 34]:

$$PhCN + MN(SiMe_3)_2 \longrightarrow M[PhC(NSiMe_3)_2]. \qquad (3)$$

$$M = K\ (\mathbf{3}),\ Rb\ (\mathbf{4}),\ Cs\ (\mathbf{5})$$

The derivative chemistry of **3**–**5** has not been further investigated, although the potassium salt may have some advantages in reactions with transition metal halides because of the low solubility of the potassium halide by-products which could facilitate their separation.

The molecular structures of two representative examples of alkali metal *N*,*N'*-bis(trimethylsilyl)benzamidinates have been determined by X-ray diffraction [34]. In an earlier study hints were obtained from spectroscopic data that these salts might be dimeric in the solid state. For example, the mass spectrum of **2** (R = H) showed the molecular ion of a dimeric unit with high relative intensity [30]. The assumption of dimeric structures was later confirmed by X-ray analyses of $[MeC_6H_4C(NSiMe_3)_2Li(THF)]_2$ (**6**) and $[PhC(NSiMe_3)_2Na(Et_2O)]_2$ (**7**) [34]. These two well-defined solvates were obtained by recrystallization of **1** (R = Me) and **2** (R = H) from THF and diethylether respectively at low temperatures. Single crystals of both solvated benzamidinates are thermally labile and decompose below room temperature. Both compounds are dimeric in the solid state but the molecular structures are strongly influenced by the alkali metal used. For **6** a "ladder structure" was found (Fig. 1), which is also characteristic for a number of alkali metal alkoxysilylamides [35, 36] and alkali metal diiminosulfinates [37, 38].

A folded array of three four-membered ring systems constitutes the central part of the molecule. The dihedral angles between the outer CN_2Li rings and the inner Li_2N_2 ring are 130.4° and 145.3° respectively. The central Li_2N_2 ring is not planar but folded by 26.3° around the Li(1)···Li(2) vector. An important structural detail is the orientation of the phenyl rings, which are in a perpendicular arrangement with respect to the NCN heteroallylic units. This orientation does not allow any significant conjugation between the two π-systems.

In **7** two chelating benzamidinate anions are centered around a nearly linear O-Na-Na-O unit (Fig. 2) [34]. With 2.741(4) Å the Na(1)···Na(2) distance is the shortest Na···Na contact found in any organometallic compound containing sodium.

The coordination sphere of the sodium atoms is completed by diethylether molecules. Once again the orientation of the phenyl substituents is perpendicular with respect to the heteroallylic NCN system.

The use of differently substituted *p*-benzonitriles in the preparation of *N*-silylated benzamidine derivatives allows a variation of the electronic properties. However, substituents in the *para* position of the phenyl ring do not significantly influence the steric demand of the resulting anions. For the design of versatile new ligand systems it is important to have the possibility of fine-tuning the steric bulk by introduction of substituents. Sterically highly demanding *N*-silylated benzamidinate anions were prepared using a different synthetic approach [30]. This method uses bis(trimethylsilyl)carbodiimide as a reagent to introduce the $C(NSiMe_3)_2$ unit. The reagent is easily accessible in large quantities via silylation of cyanamide [39]. Nucleophilic addition of mesityllithium [40] or 2,4,6-tris(trifluoromethyl)phenyllithium [41] to

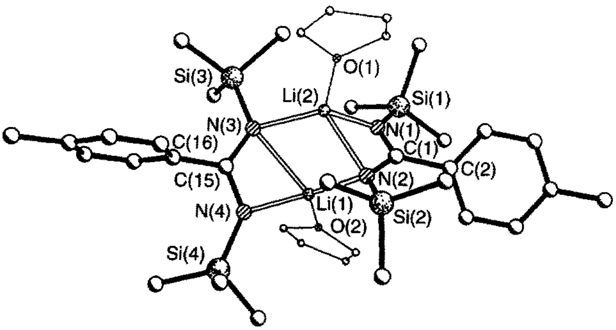


Fig. 1. Molecular structure of $[MeC_6H_4C(NSiMe_3)_2Li(THF)]_2$ (**6**)

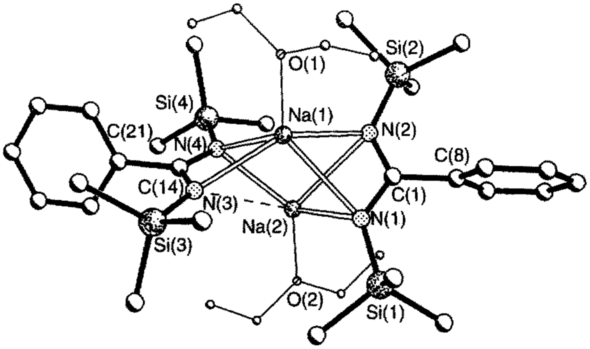


Fig. 2. Molecular structure of $[PhC(NSiMe_3)_2Na(Et_2O)]_2$ (**7**)

$Me_3SiN{=}C{=}NSiMe_3$ directly yields the lithium salts **8** in one step:

$$2,4,6\text{-}R_3C_6H_2Li + Me_3SiN{=}C{=}NSiMe_3 \longrightarrow Li[2,4,6\text{-}R_3C_6H_2C(NSiMe_3)_2]. \qquad (4)$$

$$\mathbf{8} : R = Me, CF_3$$

The lithium benzamidinates **8** can be obtained analytically pure by recrystallization from hexane. Unsolvated **8** ($R = CF_3$) is especially remarkable in that it sublimes readily at room temperature and dissolves freely in nonpolar solvents such as toluene or even hexane. Although the molecular structures of **8** ($R = CF_3$) has not been determined by X-ray diffraction, it is highly likely that the 2,4,6-tris(trifluoromethyl)phenyl substituent is responsible for the remarkable properties of this particular lithium benzamidinate. It has been demonstrated that the stabilizing influence of the 2,4,6-tris(trifluoromethyl)phenyl substituent can be traced back to a combination of steric and electronic effects [42]. In addition, this ligand allows the characterization of its derivatives by ^{19}F NMR spectroscopy.

The preparation of the sulfur analogue Li[PhS(NSiMe$_3$)$_2$] (**9**) involves treatment of *N*,*N'*-bis(trimethylsilyl)sulfur diimide with phenyllithium (Eq. 5). A 2 : 1 adduct with diethylether (**10**) is isolated when the reaction is carried out in this solvent [43]:

$$\mathrm{Me_3SiN{=}S{=}NSiMe_3 + PhLi} \xrightarrow{\mathrm{Et_2O}} \underset{\mathbf{(10)}}{\mathrm{Li[PhS(NSiMe_3)_2] \cdot 0.5Et_2O.}} \qquad (5)$$

A crystal structure determination of **10** revealed the presence of a twisted tricyclic structure with both a four-coordinate and a three-coordinate lithium atom in the same aggregate (Fig. 3) [44].

The lithium salt Li[Me$_2$Si(O*t*Bu)(N*t*Bu)] (**11**) is easily obtained in a straightforward preparation starting with Me$_2$SiCl$_2$ as outlined in Scheme 2 [45].

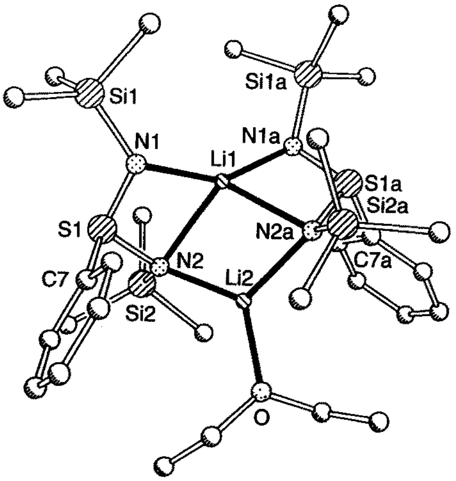
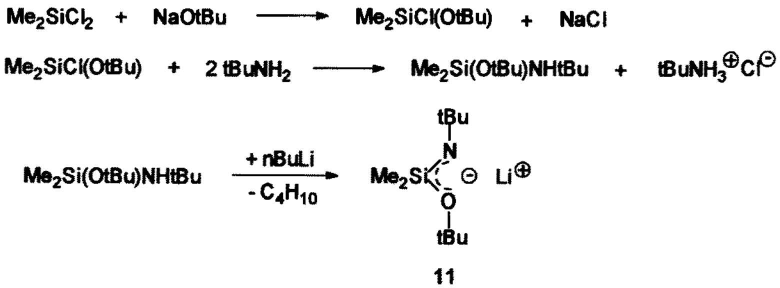


Fig. 3. Molecular structure of Li[PhS(NSiMe$_3$)$_2$] · 0.5 Et$_2$O (**10**)



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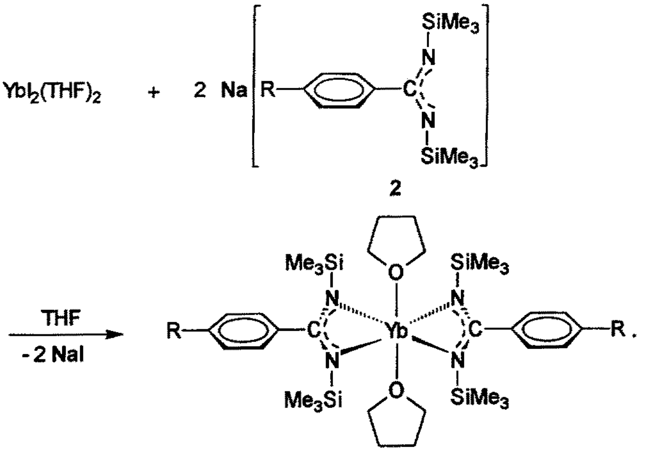
Scheme 2. Preparation of Li[Me$_2$Si(O*t*Bu)(N*t*Bu)] (**11**)

2.2 Lanthanide(II) Derivatives

Like $C_5H_5^-$ and $C_5Me_5^-$ the heteroallylic ligands $[RC_6H_4C(NSiMe_3)_2]^-$ and $[Ph_2P(NSiMe_3)_2]^-$ have been found to give stable though highly reactive lanthanide(II) complexes [46, 47]:



(6)

12o: R = H, OMe

The complexes **12o** can be isolated as dark red, beautifully crystalline, highly air-sensitive solids, which are readily soluble in hydrocarbon solvents such as hexane or toluene. The presence of divalent ytterbium was unambiguously demonstrated by ^{171}Yb NMR spectroscopy [48]. A crystal structure determination of **12o** (R = H) revealed a distorted octahedral geometry with the THF ligands occupying the *trans* positions (Fig. 4) [46]. The dihedral angle between the two planar Si-N-C-N-Si units of the chelating ligands is 26.3° and is thus comparable with the torsion angle found in the unsolvated chromium benz-

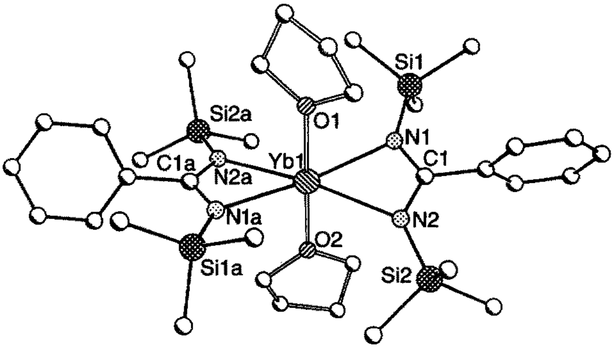
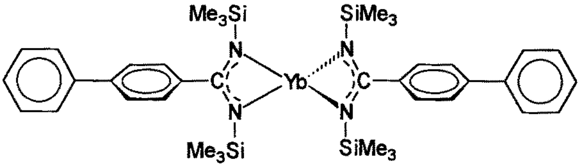


Fig. 4. Molecular structure of $[PhC(NSiMe_3)_2]_2Yb(THF)_2$ (**12o**, R = H)

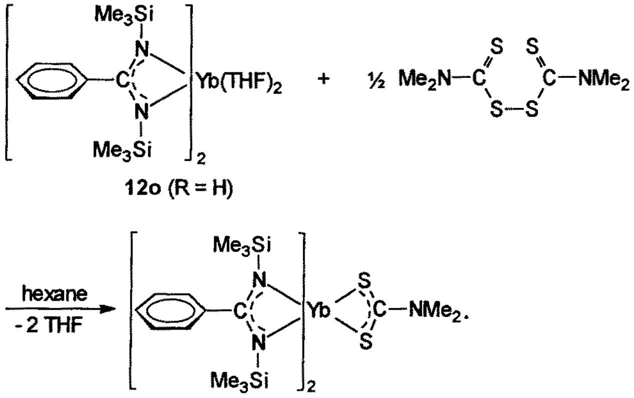
amidinate $[PhC(NSiMe_3)_2]_2Cr$ (22.8°) [49]. With an average of 2.48 Å the Yb-N bond lengths are favorably comparable with those in the anionic amido complex $Na[Yb^{II}\{N(SiMe_3)_2\}_3]$ (Yb-N 2.38 Å, 2.44 Å, 2.47 Å) [50]. A large torsion angle (77.3°) between the phenyl rings and the N-C-N units clearly indicates that conjugation between the two π-systems is negligible.

A rare example of four-coordinate ytterbium was observed in the unsolvated species $[PhC_6H_4C(NSiMe_3)_2]_2Yb$ (**13o**) [46]. Obviously the formation of solvated or unsolvated species in this system depends on subtle changes in the steric requirements of the ligands.



13o

Both complexes **12o** (R = H, OMe) are hydrocarbon-soluble and readily undergo various redox reactions, i.e. with alkyl halides, disulfides, diselenides and ditellurides. Ytterbium(II) compounds are known as strong reducing agents ($E^0(Yb^{3+}/Yb^{2+}) = -1.15$ V [51]). The reductive cleavage of E–E bonds (E = S, Se, Te) in the presence of divalent ytterbium provides a good access to lanthanide(III) complexes containing soft donor ligands. Cleavage of the sulfur–sulfur bond in $[Me_2NC(S)S]_2$ by **12o** (R = H) gave the ytterbium(III) dithiocarbamate **14o** [46]:



12o (R = H)

(7)

14o

The ytterbium(III) product **14o** was isolated as large colorless crystals in 33% yield. A comparable pentamethylcyclopentadienyl derivative, $(C_5Me_5)_2Yb(S_2CNEt_2)$ was described by Andersen et al. in 1982 [52]. The bent $[PhC(NSiMe_3)_2]_2Yb$ unit in **14o** structurally resembles the bent lanthanide metallocenes containing $(C_5Me_5)_2Ln$ moieties (Fig. 5).

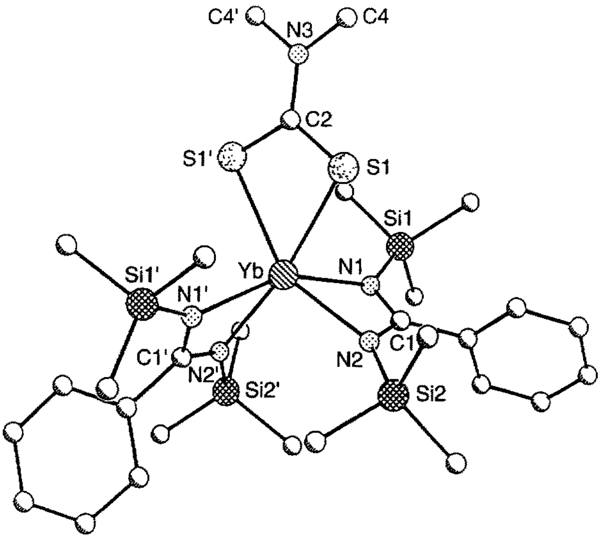
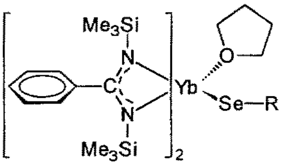


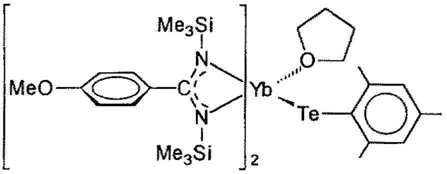
Fig. 5. Molecular structure of $[PhC(NSiMe_3)_2]_2Yb(S_2CNMe_2)$ (**14o**)

The ytterbium(III) selenolate complexes **15o** and **16o** were prepared analogously from **1** and diphenyldiselenide and dimesityldiselenide respectively [46, 47].



15o: R = Ph

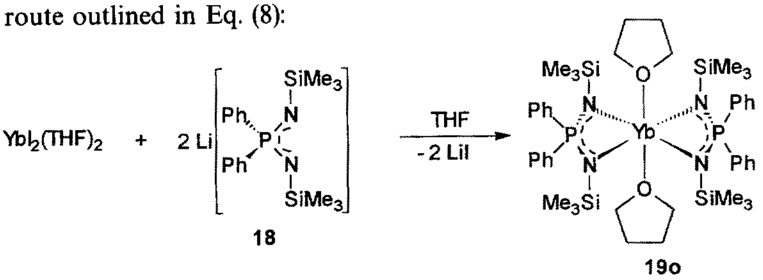
16o: R = Mes



17o

The preparation of **17o** clearly showed that even stable compounds with lanthanide-tellurium bonds are easily accessible using this method. All three complexes exhibit strongly temperature-dependent ^1H NMR spectra, which have been discussed in detail [47]. The molecular structures of both **15o** and **16o** (Fig. 6) have been determined by X-ray diffraction [46, 47].

An ytterbium(II) diiminophosphinate **19o** [53] was obtained by the synthetic route outlined in Eq. (8):



18

19o

(8)

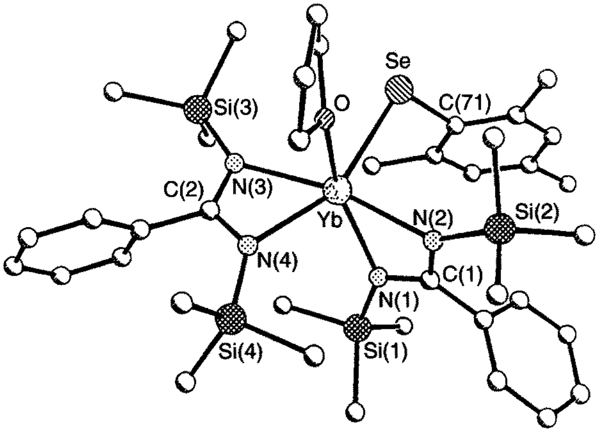


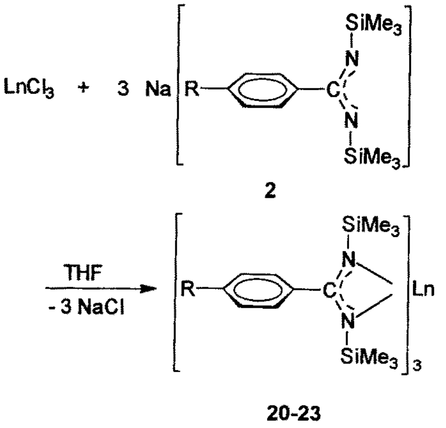
Fig. 6. Molecular structure of $[PhC(NSiMe_3)_2]_2Yb(SeMes)(THF)$ (**16o**)

^{171}Yb NMR spectroscopy has recently been shown to be a versatile tool to characterize diamagnetic complexes of divalent ytterbium [48, 54]. Generally $(C_5Me_5)_2Yb(THF)_2$ is used as a standard reference in these investigations. Compound **19o** was the first ytterbium(II) complex for which an ytterbium-phosphorus coupling constant was determined by NMR spectroscopy (**19o**: $\delta(^{171}Yb) = 521.2(d)$ ppm, $^2J_{Yb\text{-}P} = 67$ Hz) [53].

2.3 Lanthanide(III) Complexes

2.3.1 Benzamidinates

Lanthanide(III) complexes containing benzamidinate ligands represent the largest group of compounds in this area. Several benzamidinate ligands form homoleptic lanthanide complexes of the type $[RC_6H_4C(NSiMe_3)_2]_3Ln$ (**20–23**) [33] and $[PhC(NR)_2]_3Ln$ (R = *i*Pr (**24**), *c*-C_6H_{11} (**25**)) [55]. These highly soluble compounds have been described for many lanthanide elements. Equation (9) illustrates a typical preparation:



(9)

20 : R = H, Ln = Sc,Ce,Pr,Nd,Sm,Eu,Gd,Yb,Lu
21 : R = MeO, Ln = Pr,Nd,Eu,Yb,Lu
22 : R = CF_3, Ln = Sc,Pr,Nd,Eu
23 : R = Ph, Ln = Pr,Nd,Eu,Yb

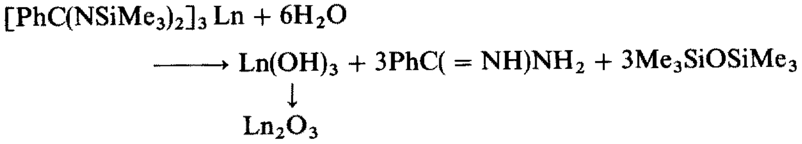
The molecular structure of the praseodymium derivative $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$ (**21e**, R = OMe) was determined by X-ray diffraction (Fig. 7) [33]. The coordination geometry in **21e** (R = OMe) was found to be distorted octahedral. The dihedral angles between the phenyl rings and the N-C-N heteroallylic units fall in the range between 66.9° and 88.6° Once again these torsion angles are too large to allow for a significant conjugation between the two π-systems. At 2.48 Å, the Pr-N distances are remarkably short compared to other structurally characterized praseodymium complexes such as $[Pr(bipy)_6](ClO_4)_3$(Pr-N 2.735–2.768 Å [56]) or $[Pr(terpy)Cl(H_2O)_5]Cl_2$ (Pr-N 2.625–2.635 Å [57]).

In addition to structural investigations, the homoleptic complexes **20–23** have been thoroughly studied using various spectroscopic techniques [33, 58]. On the basis of absorption and emission measurements the crystal field splitting patterns for $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$ (**21e**) and $[MeOC_6H_4C(NSiMe_3)_2]_3Eu$ (**21h**) were derived. The data indicate that the *N*,*N'*-bis(trimethylsilyl)benzamidinate ligand can be considered to a certain extent as an electronic equivalent to the $C_5H_5^-$ ligand in the case of Ln central ions with small electron affinity [58].

All *N*-silylated lanthanide tris(benzamidinates) **20–23** are highly soluble in non-polar solvents such as toluene, pentane, or hexane. This can be attributed to the presence of six trimethylsilyl groups which effectively shield the central lanthanide ion and make the molecules highly lipophilic. Due to their high solubility in organic solvents the homoleptic lanthanide benzamidinates $[PhC(NSiMe_3)_2]_3Ln$ (**20**) are promising precursors for lanthanide based materials. The formation of lanthanide oxides Ln_2O_3 using the sol-gel technique has been studied (Scheme 3) [55]:

Preliminary experimental results indicate that other lanthanide chalcogenides (Ln_2S_3, Ln_2Se_3) may also be accessible by a similar procedure in which the complexes **20** are treated in inert solvents with H_2S or H_2Se, respectively [38].

The homoleptic lanthanide(III) benzamidinates **20–23** can be regarded as analogues of the well known tris(cyclopentadienyl)lanthanide complexes $(C_5H_5)_3Ln$ [7, 8]. One of the most characteristic reactions of the homoleptic cyclopentadienyls is the formation of 1 : 1 adducts with Lewis bases such as ethers, nitriles, esters etc. [7, 8]. Recently it was discovered that the homoleptic lanthanide benzamidinates $[PhC(NSiMe_3)_2]_3Ln$ (**20**) form similar adducts with THF and nitrile ligands such as acetonitrile or benzonitrile [59]. The molecular and crystal structures of two benzonitrile adducts (**26g, h**) have been determined by X-ray diffraction. Figure 8 depicts the molecular structure of the europium



$$\begin{array}{l} [PhC(NSiMe_3)_2]_3\,Ln + 6H_2O \\ \qquad \longrightarrow Ln(OH)_3 + 3PhC(=NH)NH_2 + 3Me_3SiOSiMe_3 \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\quad Ln_2O_3 \end{array}$$

Scheme 3. Sol-gel preparation of Ln_2O_3 from $[PhC(NSiMe_3)_2]_3Ln$ (**20**)

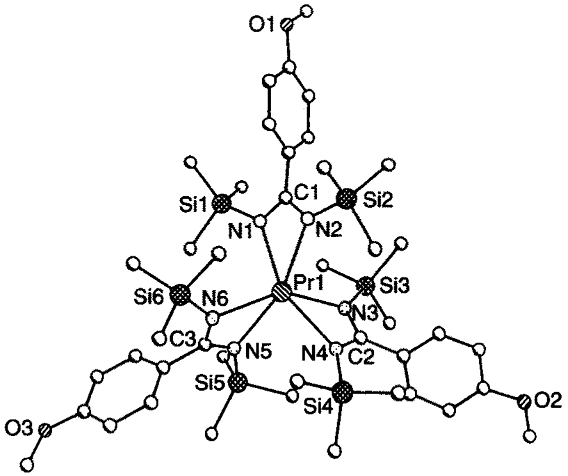


Fig. 7. Molecular structure of $[MeOC_6H_4C(NSiMe_3)_2]_3Pr$ (**21e**)

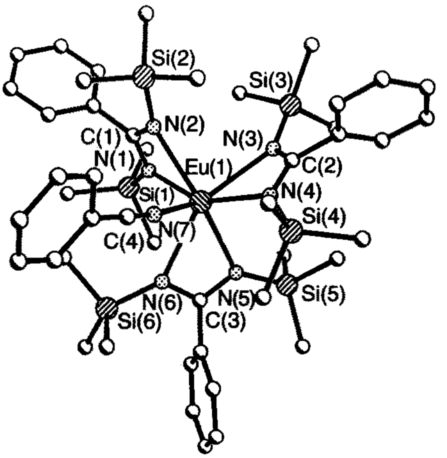
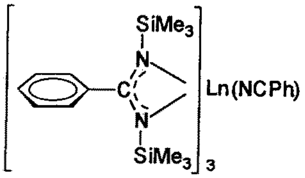


Fig. 8. Molecular structure of $[PhC(NSiMe_3)_2]_3Eu(NCPh)$ (**26h**)

derivative **26h**. The most surprising aspect is that even the three bulky benzamidinate ligands obviously leave enough room in the coordination sphere of the lanthanide anions that addition of "slim" ligands such as acetonitrile or benzonitrile is possible.



26g,h (Ln = Sm,Eu)

Due to the presence of both Ln–N and Si–N bonds in the molecules, lanthanide complexes containing the *N*-silylated benzamidinate ligands $[RC_6H_4C(NSiMe_3)_2]^-$ are highly unstable with respect to hydrolysis (see above). In some cases, i.e. the above-mentioned sol-gel process, this property is desirable while for other applications, such as in homogeneous catalysis, hydrolytic instability is certainly a disadvantage. In order to prepare lanthanide benzamidinates which are less prone to hydrolysis the *N*-alkylated ligands $[PhC(N\textit{i}Pr)_2]^-$ and $[PhC(N\text{-}c\text{-}C_6H_{11})_2]^-$ have been developed. Both ligands are easily accessible in the form of their lithium salts by treatment of the appropriate *N*,*N'*-dialkylcarbodiimides with one equivalent of phenyllithium [60]:

$$\text{R-N=C=N-R} + \text{PhLi} \longrightarrow \text{Li[PhC(NR)}_2]. \qquad (10)$$

27: $R = iPr$

28: $R = c\text{-}C_6H_{11}$

The corresponding homoleptic lanthanide tris(benzamidinates) are accessible in a straightforward manner by reacting anhydrous lanthanide trichlorides with the lithium salts in a 1:3 molar ratio [60]:

$$\text{LnCl}_3 + 3\text{Li[PhC(NR)}_2] \longrightarrow [\text{PhC(NR)}_2]_3\text{Ln}. \qquad (11)$$

24: $R = iPr$, Ln = Pr,Nd,Sm

25: $R = c\text{-}C_6H_{11}$, Ln = Pr,Nd,Sm

As expected, the products **24** and **25** are significantly less sensitive toward hydrolysis than the corresponding *N*-silylated derivatives **20–23**. Structurally all these complexes are very similar as exemplified by the X-ray crystal structure analysis of **25e** (Fig. 9) [60].

In cyclopentadienyl lanthanide chemistry, disubstituted complexes are probably the most important compounds as they contain reactive halide ligands [4–8]. These can be replaced by various other substituents such as hydride, alkyl, amide or alkoxide ligands. Thus the bis(cyclopentadienyl)lanthanide chlorides represent one of the most versatile classes of reactive precursors in organolanthanide chemistry. These compounds exist in several different structural types depending on the size of the ligands and on the ionic radius of the lanthanide element [7, 8]. In the case of the unsubstituted cyclopentadienyl ligand, dimeric complexes of the type $[Cp_2LnCl]_2$ can be isolated for almost any lanthanide element. For $C_5Me_5^-$ and other bulky substituted cyclopentadienyl ligands (e.g. $(Me_3Si)_2C_5H_3^-$, $tBu_2C_5H_3^-$), chloride-bridged dimers have been isolated with the early lanthanide elements. In some cases the THF solvates $(C_5Me_5)_2LnCl(THF)$ are formed. Obviously the fragments $(C_5Me_5)_2LnCl$ (coordination number 7) are coordinatively unsaturated and exhibit a strong tendency to increase the coordination number around the lanthanide atom. Formal eight-coordination is achieved in the above-mentioned dimers and THF solvates. The third possibility is the formation of "ate" complexes through incorporation of lithium halide. This results in complexes of the general type

$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(S)_2$ where S is a solvent molecule such as diethyl ether, THF or 1/2 DME. These compounds containing a four-membered $Ln(\mu\text{-}Cl)_2Li$ ring are very characteristic and common in pentamethylcyclopentadienyl lanthanide chemistry. In fact, this type of complex was known originally only for organolanthanide complexes containing the $C_5Me_5^-$ ligand [4–8]. Thus it was an important finding that the bulky heteroallylic ligands are able to form very similar disubstituted lanthanide(III) complexes containing a four-membered $Ln(\mu\text{-}Cl)_2Li$ ring as the central structural unit. Together with numerous other analogies it confirms the theory that the *N*-silylated heteroallylic ligands are steric cyclopentadienyl equivalents, especially in the case of lanthanide and actinide elements [27, 30, 33, 42, 61].

Just as the $(C_5Me_5)_2LnCl$ derivatives are highly useful precursors in organolanthanide chemistry the bis(benzamidinate)lanthanide chlorides should also develop into some very useful starting materials. Thus considerable research effort is currently being directed towards rational syntheses of these compounds. For many metal/ligand combinations it was found that the homoleptic lanthanide benzamidinates $[RC_6H_4C(NSiMe_3)_2]_3Ln$ were the preferred reaction products. In these cases mixtures of products were obtained when the reactions were carried out in a 2 : 1 ligand-to-metal molar ratio. From this it was concluded that two factors should increase the chance of isolating pure disubstitution products. Disubstitution should be more favorable if either very bulky ligands are used (i.e. $[(CF_3)_3C_6H_2C(NSiMe_3)_2]^-$) or if the ionic

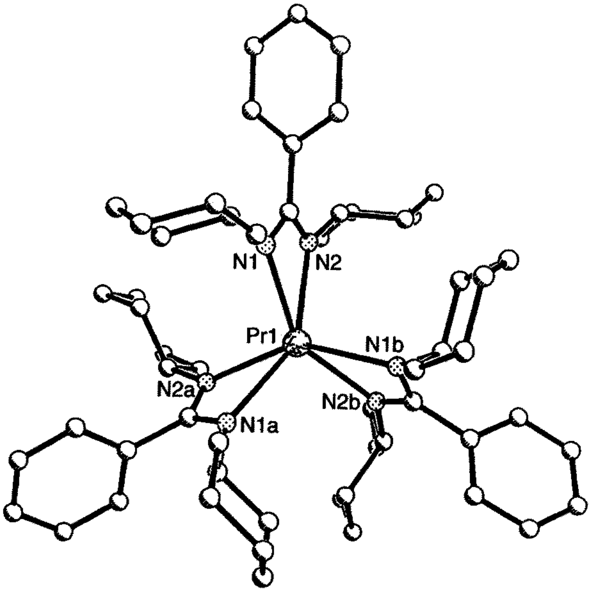
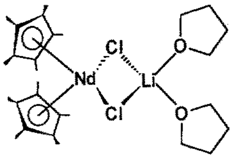


Fig. 9. Molecular structure of $[PhC(N\text{-}c\text{-}C_6H_{11})_2]_3Pr$ (**25e**)

radius of the metal ion is small (i.e. Sc, Y, Yb, Lu). Both assumptions were subsequently confirmed through experiments.

In an early paper Wayda and Evans reported that LiC_5Me_5 reacts with anhydrous neodymium trichloride in refluxing THF to give exclusively the disubstituted complex **29f** [62]:

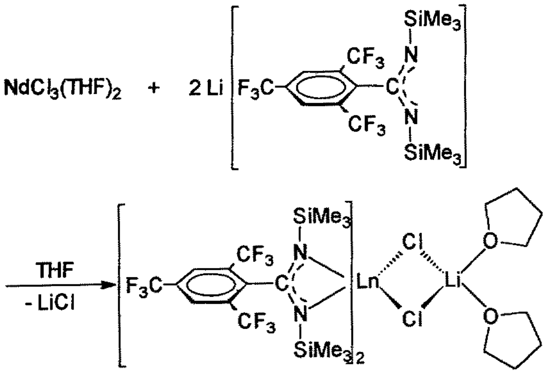
$$NdCl_3 + 2\,LiC_5Me_5 \xrightarrow[\text{- LiCl}]{\text{THF}} \underset{\textbf{29f}}{(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2} . \qquad (12)$$



29f

Compound **29f** is formally an "ate" complex in which one equivalent of LiCl is retained in the product in order to increase the coordination number at the neodymium atom. Neodymium and lithium are bridged by two chlorine atoms and the coordination sphere at lithium is completed by two THF ligands.

An entirely analogous reaction occurs when anhydrous neodymium trichloride is reacted under similar conditions with two equivalents of $Li[(CF_3)_3C_6H_2C(NSiMe_3)_2]$. In this reaction (Eq. 13) the very bulky benzamidinate ligand behaves like a steric equivalent of $C_5Me_5^-$ [63]:



(13)

30f

The molecular structure of **30f** was confirmed by X-ray diffraction [63]. Just as in the corresponding C_5Me_5 derivatives, a four-membered $Nd(\mu\text{-}Cl)_2Li$ ring constitutes the central part of the molecule (Fig. 10).

An unusual molecular array was obtained upon recrystallization of **30f** from dimethoxyethane. In the resulting binuclear neodymium complex **31f** two THF ligands are replaced by a bridging DME ligand (Fig. 11) [63].

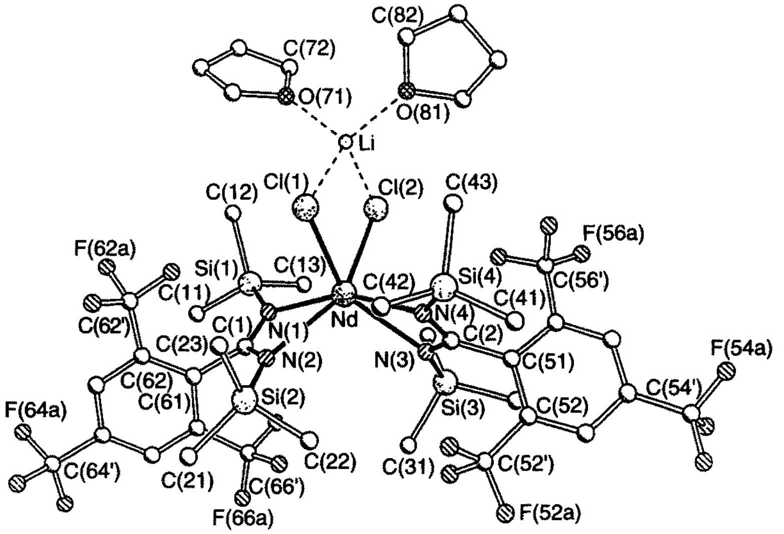


Fig. 10. Molecular structure of $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ (**30f**)

Initial reactivity studies showed that **13** can serve as a useful starting material for further reactions [64]. For example, the reactive chlorine atom can be replaced by amido or alkyl ligands such as $N(SiMe_3)_2$ or $CH(SiMe_3)_2$ to give the products $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2NdN(SiMe_3)_2$ (**32f**) and $[(CF_3)_3C_6H_2C(NSiMe_3)_2]_2NdCH(SiMe_3)_2$ (**33f**) respectively. These correspond to the known organoneodymium complexes $(C_5Me_5)_2NdN(SiMe_3)_2$ and $(C_5Me_5)_2NdCH(SiMe_3)_2$.

Once again the typical chloro-bridged "ate" complex known so far only from C_5Me_5 lanthanide chemistry was realized with a bulky chelating ligand. This example clearly showed that the selective formation of disubstituted complexes could also be achieved by adjusting the steric requirements of the ligands to the ionic radius of the metal atom. To test this hypothesis, scandium and yttrium were chosen to synthesize well-defined complexes of the type $[RC_6H_4C(NSiMe_3)_2]_2LnCl(THF)$ (**34a**, **35b**: Ln = Sc,Y), i.e. with the use of sterically less demanding benzamidinate ligands. Indeed, treatment of either $ScCl_3(THF)_3$ or $YCl_3(THF)_{3.5}$ with two equivalents of the silylated benzamidinate ligands resulted in a clean formation of the desired disubstitution products [27, 55, 65, 66]:

$$ScCl_3(THF)_3 + 2Li[RC_6H_4C(NSiMe_3)_2]$$

$$\mathbf{1}$$

$$\xrightarrow[-\,2LiCl]{THF} [RC_6H_4C(NSiMe_3)_2]_2ScCl(THF) \qquad (14)$$

$$\mathbf{34a}\text{: } R = H,MeO,CF_3$$

$$\underset{\mathbf{1}}{\mathrm{YCl_3(THF)_{3.5} + 2Li[RC_6H_4C(NSiMe_3)_2]}} \xrightarrow[-\,2\mathrm{LiCl}]{\mathrm{THF}} \underset{\mathbf{35b:\ R = H, MeO, CF_3}}{\mathrm{[RC_6H_4C(NSiMe_3)_2]_2YCl(THF)}}. \qquad (15)$$

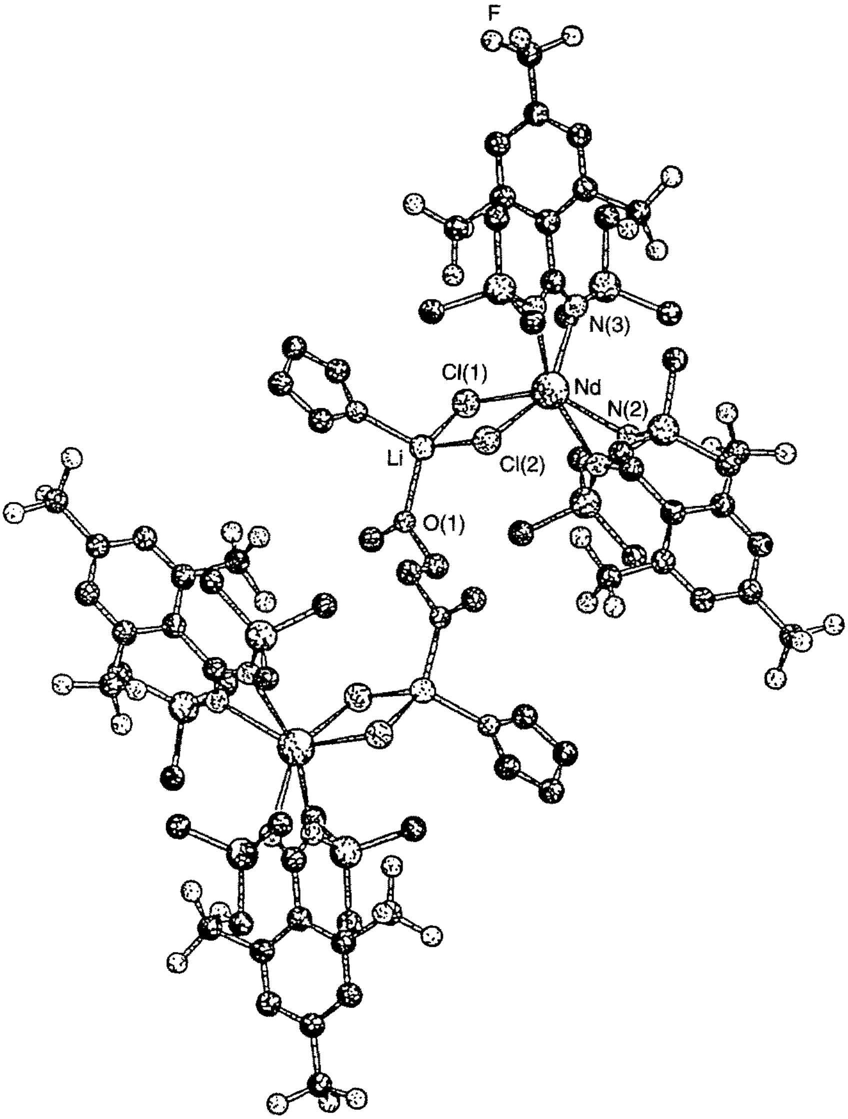
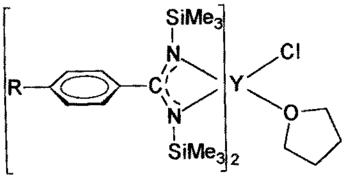


Fig. 11. Molecular structure of $(\mu\text{-DME})[\{(CF_3)_3C_6H_2C(NSiMe_3)_2\}_2Nd(\mu\text{-Cl})_2Li(THF)]_2$ (**31f**)



35b (R = H,MeO,CF_3)

The products **34a** and **35b** were isolated as colorless, crystalline solids. In the case of the reaction of $YCl_3(THF)_{3.5}$ with two equivalents of $Li[PhC(NSiMe_3)_2]$ the initially formed product is the ate-complex $[PhC(NSiMe_3)_2]_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (**36b**) which results from lithium chloride incorporation into the monochloride complex [27]. Attempts to remove the LiCl and THF by sublimation under vacuum failed. However, the coordinated LiCl can easily be removed by treatment of the ate-complex with refluxing pentane which affords the THF adduct $[PhC(NSiMe_3)_2]_2YCl(THF)$. Even higher yields (ca. 80–90%) of such disubstituted complexes are obtained when anhydrous yttrium triflate is used as precursor. Treatment of $Y(O_3SCF_3)_3$ with two equivalents of $Li[RC_6H_4C(NSiMe_3)_2]$ yields the novel bis(ligand) yttrium triflates **37b** [55, 66]:

$$Y(O_3SCF_3)_3 + 2\ \underset{\mathbf{1}}{Li[RC_6H_4C(NSiMe_3)_2]}$$

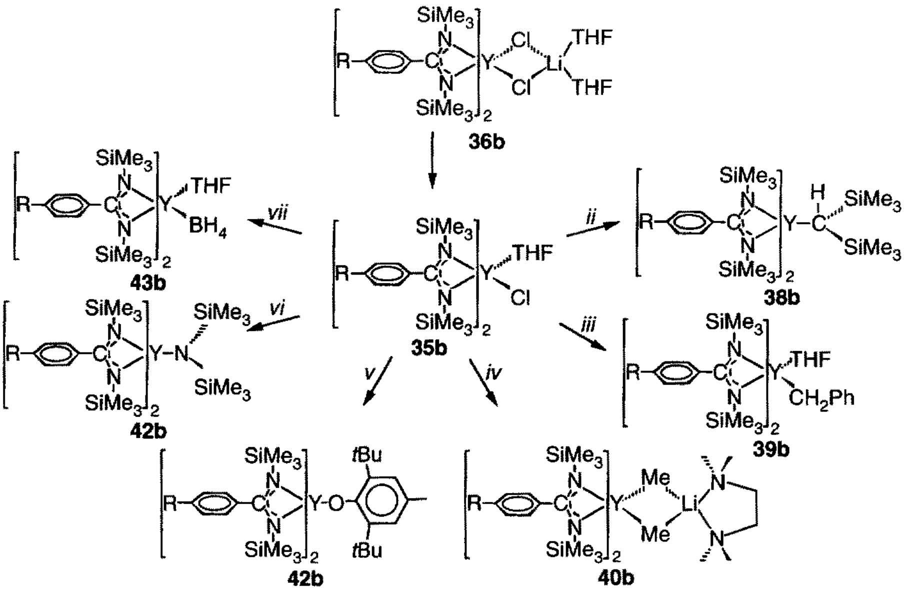
$$\xrightarrow[-\,2LiO_3SCF_3]{THF} [RC_6H_4C(NSiMe_3)_2]_2Y(O_3SCF_3). \qquad (16)$$

37b: R = H,MeO,CF_3

All these new scandium and yttrium complexes can also serve as versatile starting materials for various derivatives including highly reactive alkyl and hydride species [27, 55, 65, 66]. For example, the chlorine atom in **34a** and **35b** is easily replaced by various anionic ligands such as OAr, $N(SiMe_3)_2$ or $CH(SiMe_3)_2$ [27]. The derivative chemistry of $[PhC(NSiMe_3)_2]_2YCl(THF)$ is illustrated in Scheme 4. Thus far the use of scandium and yttrium appears to be the best entry into the chemistry of disubstituted complexes with bulky heteroallylic ligands. More recently it was found that the yttrium triflates **37b** are even better suited for this type of substitution reaction because LiO_3SCF_3 is more easily separated from the reaction mixtures than LiCl [55, 66].

The most interesting species in this series are certainly the yttriumalkyls **38b** which have been prepared either from **35b** or **37b** by treatment with $LiCH(SiMe_3)_2$ in toluene solution. These alkyl derivatives **38b** are very soluble in nonpolar organic solvents and highly reactive towards various substrates such as terminal alkynes, alcohols, thiols etc. [27]. An X-ray crystal structure determination has been performed on the *p*-methoxy derivative $[MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**38b**, R = MeO) (Fig. 12) [27].

In this case the high quality of the data set allowed the determination and refinement of all hydrogen positions. This alkyl derivative is monomeric in the



Scheme 4. Derivative chemistry of $[RC_6H_4C(NSiMe_3)_2]_2YCl(THF)$ (**35b**). (*i*) pentane, reflux; (*ii*) $LiCH(SiMe_3)_2$, toluene; (*iii*) KCH_2Ph, toluene; (*iv*) MeLi, TMEDA, ether; (*v*) $LiO\text{-}2,6\text{-}tBu_2\text{-}4\text{-}MeC_6H_2$, toluene; (*vi*) $NaN(SiMe_3)_2$, toluene; (*vii*) $LiBH_4$, toluene

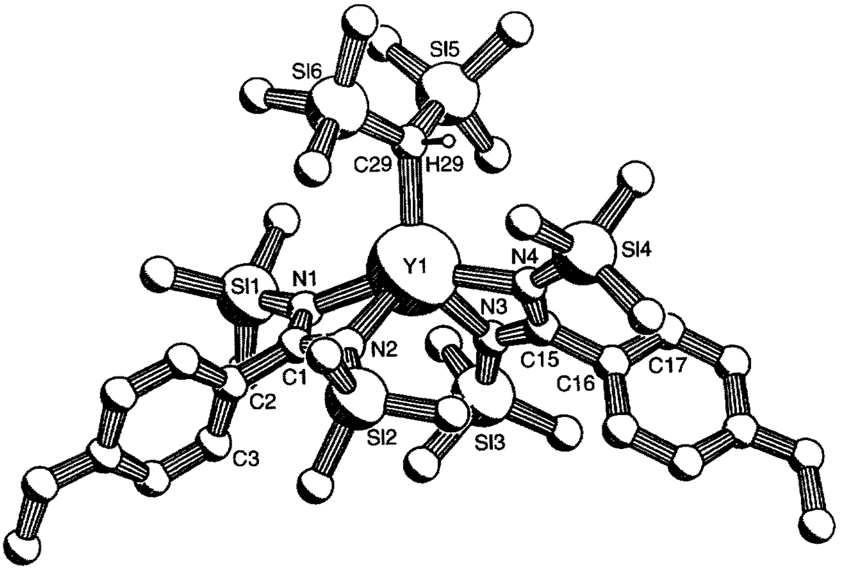
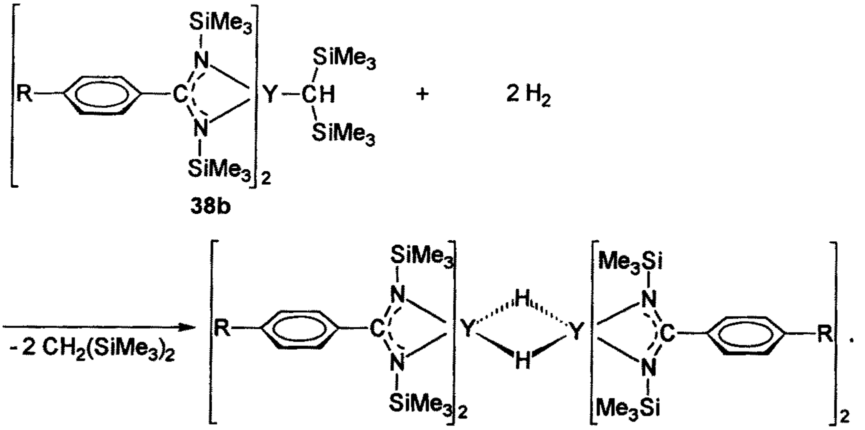


Fig. 12. Molecular structure of $[MeOC_6H_4C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**38b**, R = MeO)

solid state. The coordination geometry around the central yttrium atom can be best described as trigonal-planar, if the benzamidinate ligands are considered to occupy one vertex of the coordination polyhedron. With torsion angles of

− 2.2° and − 1.4° the four-membered YNCN-rings are both planar. The yttrium-carbon σ-bond (2.431(5) Å) is significantly shorter than that in $(C_5Me_5)_2YCH(SiMe_3)_2$ (2.468(7) Å) [67], but comparable to the Y-C distance in $(C_5Me_5)_2YMe(THF)$ (2.44(2) Å) [68]. Characteristic for all structurally investigated lanthanide bis(trimethylsilyl)methyl complexes [7, 8] is the almost planar geometry around the σ-bonded carbon atom (**38b**, R = MeO: angle sum 353.5°(2)).

Hydrogenation of **38b** under mild conditions yields the dimeric yttrium hydrides **44b** (Eq. 17). The benzyl derivatives **39b** can also be used as starting materials, but the rate of hydrogenolysis is considerably slower due to the presence of coordinated THF. The dimeric hydrides are extremely sensitive towards oxygen and moisture but thermally quite stable [27, 55, 65, 66].



38b

44b: R = H,MeO,CF$_3$

(17)

The molecular and crystal structure of **44b** (R = H) has been determined by X-ray diffraction. The molecule is a dimer formed by two edge-sharing, distorted octahedral $[Ph(NSiMe_3)_2]_2Y$ fragments, in which the central yttrium atoms are coordinated by two chelating benzamidinate ligands and two bridging hydrogen atoms in the shared edge (Fig. 13) [27].

The hydrides **44b** have been found to polymerize ethylene and react with a variety of protic reagents such as terminal alkynes and nitriles. Catalytic effects in the hydroboration of olefins have also been observed [27]. A well-defined μ-ethynyl complex of yttrium is formed by protolysis of the alkyl derivative **38b** with acetylene (Eq. 18). Figure 14 shows the dimeric structure of **45b** with bridging ethynyl ligands [27, 65].

$$\underset{\textbf{38b}\ (R=H)}{2[PhC(NSiMe_3)_2]_2YCH(SiMe_3)_2} + 2HC{\equiv}CH \longrightarrow \underset{\textbf{45b}}{[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}C{\equiv}CH)]_2} + 2CH_2(SiMe_3)_2. \qquad (18)$$

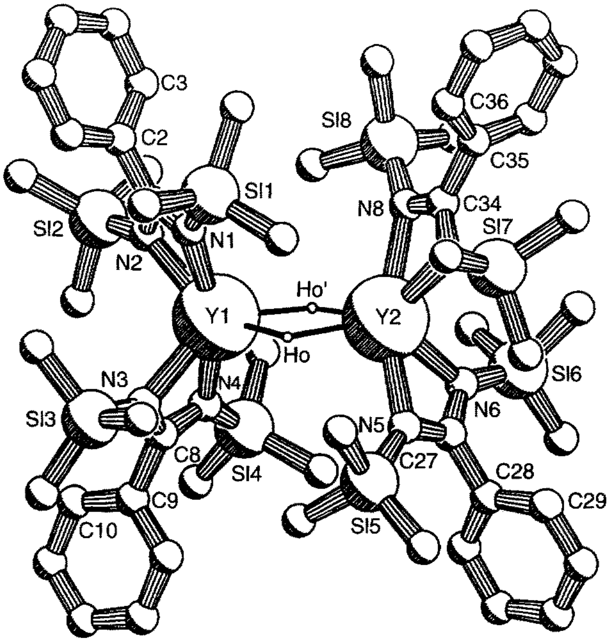


Fig. 13. Molecular structure of $[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}H)]_2$ (**44b**, R = H)

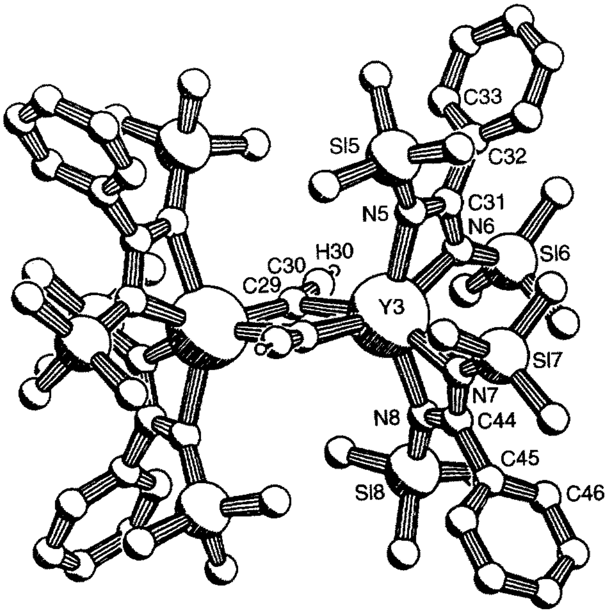


Fig. 14. Molecular structure of $[\{PhC(NSiMe_3)_2\}_2Y(\mu\text{-}C{\equiv}CH)]_2$ (**45b**)

A recent development in this field involves the combination of benzamidinate ligands with cyclopentadienyl or cyclooctatetraenyl ligands in the coordination sphere of lanthanide ions. The first lanthanide complexes containing both benzamidinate and pentamethylcyclopentadienyl bonded to yttrium was reported by Teuben et al. Yttrium aryloxides as well as anhydrous yttrium trichloride can be used as starting materials in these preparations (Eq. 19, Scheme 5) [27]:

$$(C_5Me_5)Y(OAr)_2 + \underset{\mathbf{1}\ (R=H)}{Li[PhC(NSiMe_3)_2]} \longrightarrow \underset{\mathbf{46b}}{\underset{(Ar=2,6\text{-di-}t\text{-butylphenyl})}{[PhC(NSiMe_3)_2](C_5Me_5)YOAr}} + LiOAr. \tag{19}$$

The bridging chloride ligands in **47b** can be replaced by methyl groups upon treatment with two equivalents of MeLi in the presence of TMEDA (= *N,N,N′,N′*-tetramethylethylenediamine) to afford the methyl-bridged complex $[PhC(NSiMe_3)_2](C_5Me_5)Y(\mu\text{-}Me)_2Li(TMEDA)$ (**48b**). This product was structurally characterized by an X-ray diffraction study (Fig. 15) [27]. The

$$YCl_3(THF)_{3.5} + KC_5Me_5 \xrightarrow[-\,KCl]{} (C_5Me_5)Y(\mu\text{-}Cl)_3K(THF)_n \xrightarrow[-\,LiCl]{Li[PhC(NSiMe_3)_2]} 1/2[\{PhC(NSiMe_3)_2\}(C_5Me_5)Y(\mu\text{-}Cl)]_2$$

47b

Scheme 5. Two-step preparation of $[\{PhC(NSiMe_3)_2\}(C_5Me_5)Y(\mu\text{-}Cl)]_2$ (**47b**)

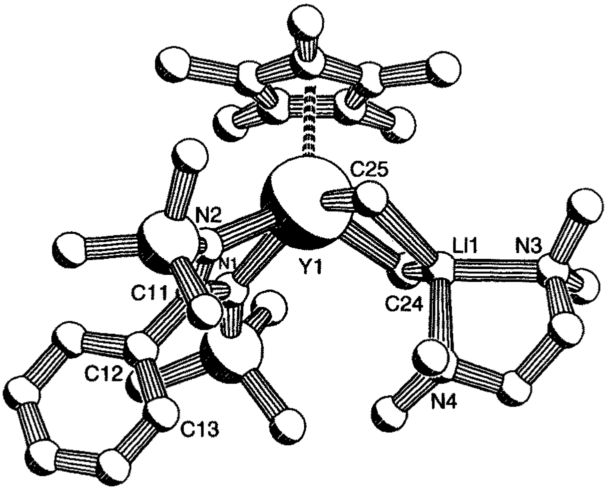


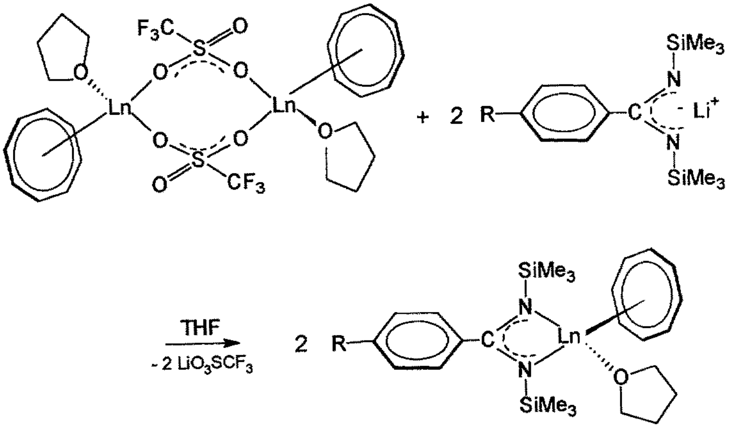
Fig. 15. Molecular structure of $[PhC(NSiMe_3)_2](C_5Me_5)Y(\mu\text{-}Me)_2Li(TMEDA)$ (**48b**)

central yttrium atom is coordinated by one pentamethylcyclopentadienyl, one benzamidinate and two methyl groups with the latter acting as bridging ligands between yttrium and lithium. The overall structure closely resembles that of the previously described mixed-ligand complexes $[PhC(NSiMe_3)_2](C_5H_5)ZrCl_2$ [69] and $[PhC(NSiMe_3)_2](C_5H_5)TiMe_2$ [70].

Protolysis of the bridging methyl groups in **48b** with *t*-butylacetylene results in stepwise formation of the μ-alkynyl derivatives **49b** and **50b** (Scheme 6) [27].

Similar treatment of $[PhC(NSiMe_3)_2](C_5Me_5)Y(\mu\text{-}Me)_2Li(TMEDA)$ (**48b**) with two equivalents of 2,6-di-*t*-butylphenol affords the monomeric mixed-ligand phenoxide derivative $[PhC(NSiMe_3)_2](C_5Me_5)YOAr$ (**51b**, Ar = 2,6-di-*t*-butylphenyl) [27]. Interestingly no competitive protolysis of the C_5Me_5 or benzamidinate ligands was observed in these reactions, indicating the high stability of the ligand environment in the $[PhC(NSiMe_3)_2](C_5Me_5)Y$ unit.

Benzamidinate and η^8-cyclooctatetraenyl ligands have also been successfully combined in the coordination sphere of lanthanide ions [71]. The preparative route to such compounds involves treatment of dimeric (η^8-cyclooctatetraenyl)lanthanide triflates with stoichiometric amounts of lithium *N*,*N'*-bis(trimethylsilyl)benzamidinates:



(20)

52: R = H, Ln = Y,Ce,Pr,Nd,Sm,Tm,Lu
53: R = OMe, Ln = Y,Ce,Pr,Nd,Sm,Tm,Lu
54: R = CF_3, Ln = Y, Tm, Lu

$$[PhC(NSiMe_3)_2](C_5Me_5)Y(\mu\text{-}Me)_2Li(TMEDA)$$

48b

$$\xrightarrow[-\,CH_4]{HC\equiv CtBu} [PhC(NSiMe_3)_2](C_5Me_5)Y(\mu\text{-}Me)(\mu\text{-}C\equiv CtBu)Li(TMEDA)$$

49b

$$\xrightarrow[-\,CH_4]{HC\equiv CtBu} [PhC(NSiMe_3)_2](C_5Me_5)Y(\mu\text{-}C\equiv CtBu)Li(TMEDA)$$

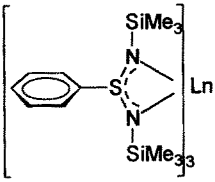
50b

Scheme 6. Successive protolysis of **48b** with *t*-butylacetylene

The compounds **52–54** can be isolated in the form of intensely colored, highly air- and moisture-sensitive crystals. X-ray crystal structure analyses have been carried out on the derivatives **52n** and **53p**. Figure 16 shows the molecular structure of the thulium derivative **52n** [71].

2.3.2 Diiminosulfinates

Homoleptic lanthanide complexes containing the $[PhS(NSiMe_3)_2]^-$ ligand were prepared in a straightforward manner by treatment of anhydrous lanthanide trichlorides with three equivalents of $Li[PhS(NSiMe_3)_2]\cdot 0.5\ Et_2O$ (**10**) [72]:



55: Ln = Sc, Nd

As expected the physical properties of the sulfur derivatives **55** are very similar to those of the corresponding lanthanide(III) benzamidinates **20**. Apparently no attempts have been made so far to prepare disubstituted lanthanide complexes containing diiminosulfinate ligands.

2.3.3 Diiminophosphinates

An interesting difference in reactivity as compared to benzamidinate chemistry was observed when anhydrous lanthanide trichlorides were reacted with three equivalents of $Li[Ph_2P(NSiMe_3)_2]$. Regardless of the stoichiometry (1:2 or 1:3)

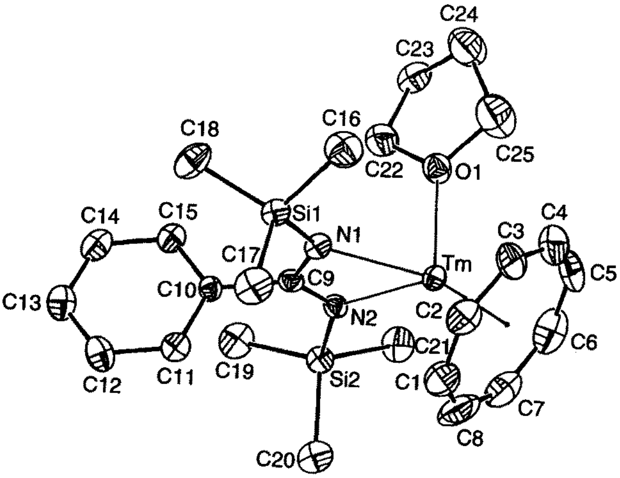
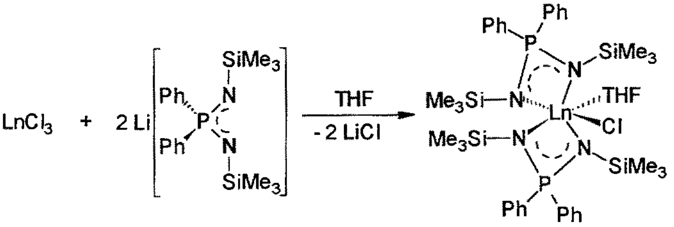


Fig. 16. Molecular structure of $[PhC(NSiMe_3)_2](C_8H_8)Tm(THF)$ (**52n**)

the disubstituted complexes **56** were found to be the only isolatable products (Eq. 21) [73]. In the exclusive formation of disubstituted products in the case of early lanthanides, the diiminophosphinate ligand $[Ph_2P(NSiMe_3)_2]^-$ very much resembles the pentamethylcyclopentadienyl ligand. In fact this was the first indication that the very bulky ligands $[(CF_3)_3C_6H_2C(NSiMe_3)_2]^-$ and $[Ph_2P(NSiMe_3)_2]^-$ might behave as steric equivalents of $C_5Me_5^-$, especially in the case of the large early lanthanide ions.

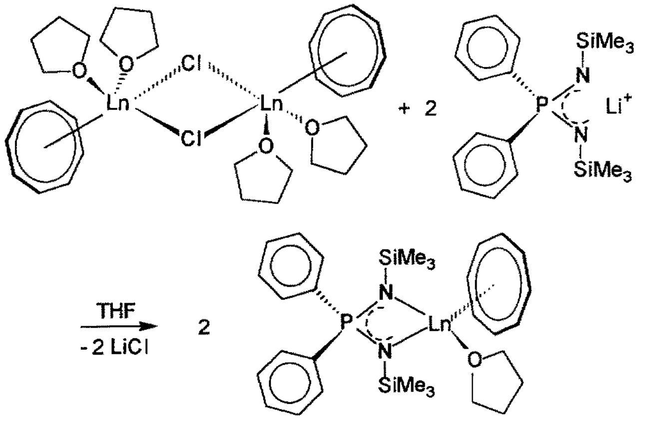


(21)

56: Ln = Pr, Nd

Samarium diiodide reacts with two equivalents of $Li[Ph_2P(NSiMe_3)_2]$ in THF with formation of a dark green solution, indicating the formation of a samarium(II) diiminophosphinate complex. However, the dark green color fades during the work-up of the reaction mixture and recrystallization of the crude product from hexane yields large, colorless crystals. This material was subsequently shown by X-ray diffraction to be the samarium(III) ate-complex $[Ph_2P(NSiMe_3)_2]_2Sm(\mu\text{-}I)_2Li(THF)_2$ (**57g**, Fig. 17). Thus samarium(II) is oxidized to the trivalent state in the course of the reaction and lithium iodide is incorporated into the product [53].

More recently several lanthanide diiminophosphinate derivatives containing additional η^8-cyclooctatetraenyl ligands have been prepared and characterized. The complexes $[Ph_2P(NSiMe_3)_2](C_8H_8)Ln(THF)$ (**58**) were obtained according to Eq. (22) and isolated as air-sensitive, crystalline solids in 77–84% yield [71]:



(22)

58: Ln = Y,Ce,Pr,Nd,Sm.

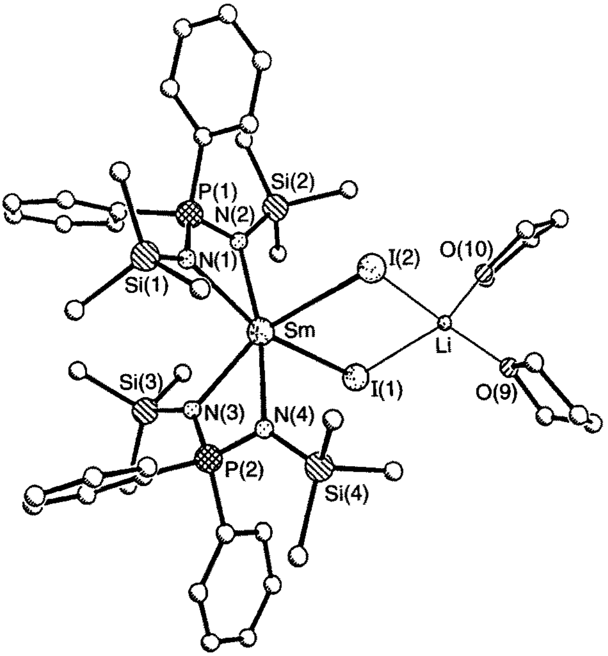


Fig. 17. Molecular structure of $[Ph_2P(NSiMe_3)_2]_2Sm(\mu\text{-}I)_2Li(THF)_2$ (**57g**)

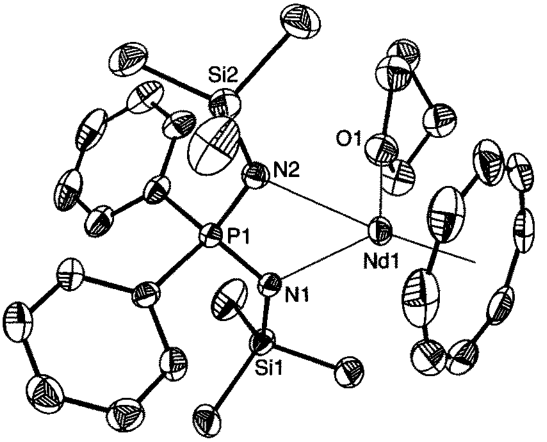


Fig. 18. Molecular structure of $[Ph_2P(NSiMe_3)_2](C_8H_8)Nd(THF)$ (**58f**)

The blue-green neodymium complex **58f** was structurally characterized by X-ray diffraction (Fig. 18). Despite the presence of both the large, flat $C_8H_8^{2-}$ ligand and the very bulky diphenyl-bis(*N*-trimethylsilylimino)phosphinate anion, the coordination sphere of neodymium leaves enough room to accomodate an additional THF ligand. The central four-membered ring formed by the neodymium atom and the NPN chelate system is nearly planar.

2.3.4 Diphosphinomethanides

An interesting class of homoleptic lanthanide complexes has become available through the use of heteroallylic diphosphinomethanide ligands. The first member of the series was the lanthanum derivative, $[CH(PPh_2)_2]_3La$ (**59c**), which was characterized by X-ray crystallography (Fig. 19) [74]. The preparation of **59c** involved treatment of anhydrous lanthanum trichloride with the potassium salt of the ligand:

$$\underset{\textbf{60}}{LaCl_3 + 3KCH(PPh_2)_2} \longrightarrow \underset{\textbf{59c}}{[CH(PPh_2)_2]_3La} + 3KCl. \qquad (23)$$

Mono- and dinuclear diphosphinomethanides have been reported for samarium(III) (Eqs. 24 and 25). Both compounds have been structurally characterized. The disamarium complex is a centrosymmetric dimer in a chair conformation with two diphosphinomethanide ligands bridging via the P(2) and C(1) atoms [75, 76]:

$$SmCl_3(THF)_3 + \underset{\textbf{61}}{3LiCH(PPh_2)_2}$$

$$\longrightarrow \underset{\textbf{62g}}{[CH(PPh_2)_2]_3Sm} + 3LiCl + 3THF \qquad (24)$$

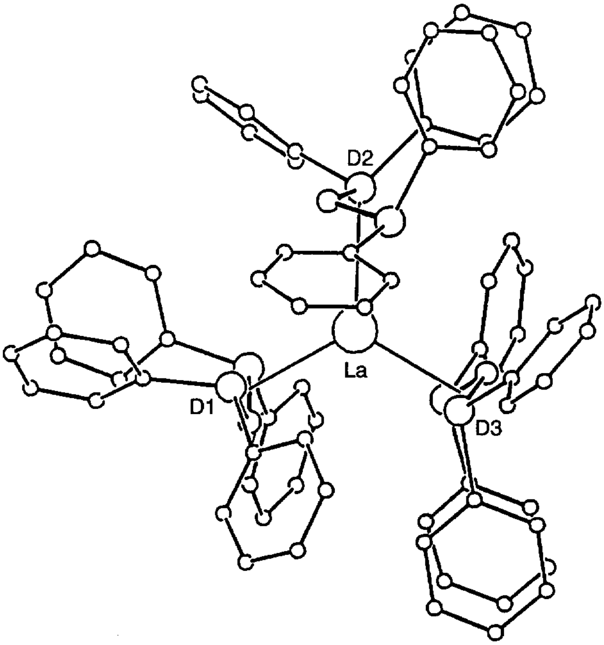


Fig. 19. Molecular structure of $[CH(PPh_2)_2]_3La$ (**59c**)

$$\mathrm{Sm(O_3SCF_3)_3} + \underset{\mathbf{63}}{\mathrm{3LiCH(PMe_2)_2}}$$

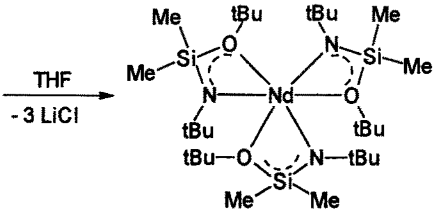
$$\longrightarrow \underset{\mathbf{64g}}{(\mu\text{-}\eta^2\text{-}\mathrm{Me_2PCHPMe_2})[\mathrm{Sm\{CH(PPh_2)_2\}_2}]_2} + \mathrm{3LiO_3SCF_3}. \qquad (25)$$

2.3.5 Alkoxysilylamides

The ionic radius of the lanthanide atom is an important factor governing the formation and successful synthesis of well-defined di- or trisubstituted complexes. This can be nicely illustrated by the example of the alkoxysilylamide ligand $[\mathrm{Me_2Si(O}t\mathrm{Bu)(N}t\mathrm{Bu)}]^-$. This anionic ligand has frequently been employed by Veith and Rösler in main group chemistry [45, 77].

The large ionic radius of neodymium as a typical representative of the early lanthanide elements allowed the formation of a homoleptic tris(alkoxysilyl amide) complex [78]:

$$\mathrm{NdCl_3(THF)_2} \quad + \quad \underset{\mathbf{11}}{\mathrm{3\ Li[Me_2Si(OtBu)NtBu]}}$$



65f

(26)

Compound **65f** was isolated as a sky-blue crystalline solid which is highly soluble in nonpolar organic solvents. The molecular structure of **65f** was determined by a single crystal X-ray analysis. It showed the neodymium atom in a distorted octahedral coordination environment (Fig. 20) [78]. Dark red crystalline $[\mathrm{Me_2Si(O}t\mathrm{Bu)(N}t\mathrm{Bu)}]_3\mathrm{Eu}$ was prepared analogously.

A marked difference in reactivity is observed with the smaller ytterbium ion. Even if an excess of the ligand is used, ytterbium trichloride reacts with $\mathrm{Li[Me_2Si(O}t\mathrm{Bu)(N}t\mathrm{Bu)]}$ selectively in a 1:2 molar ratio to give a high yield of the disubstituted product **66o** (Eq. 27, Fig. 21) [78]. Not even traces of the homoleptic complex $[\mathrm{Me_2Si(O}t\mathrm{Bu)(N}t\mathrm{Bu)}]_3\mathrm{Yb}$ were formed in this reaction:

$$\mathrm{YbCl_3} + \underset{\mathbf{11}}{\mathrm{2Li[Me_2Si(O}t\mathrm{Bu)(N}t\mathrm{Bu)]}}$$

$$\xrightarrow[-\ \mathrm{LiCl}]{\mathrm{THF}} \underset{\mathbf{66o}}{[\mathrm{Me_2Si(O}t\mathrm{Bu)(N}t\mathrm{Bu)}]_2\mathrm{Yb}(\mu\text{-}\mathrm{Cl})_2\mathrm{Li(THF)_2}}. \qquad (27)$$

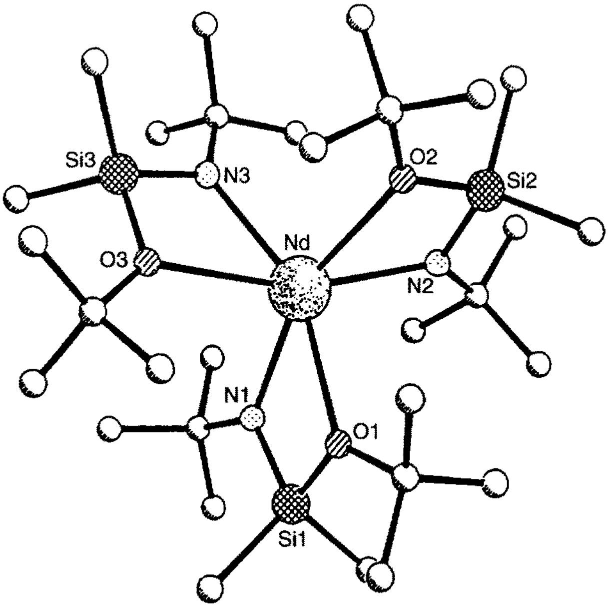


Fig. 20. Molecular structure of $[Me_2Si(OtBu)(NtBu)]_3Nd$ **(65f)**

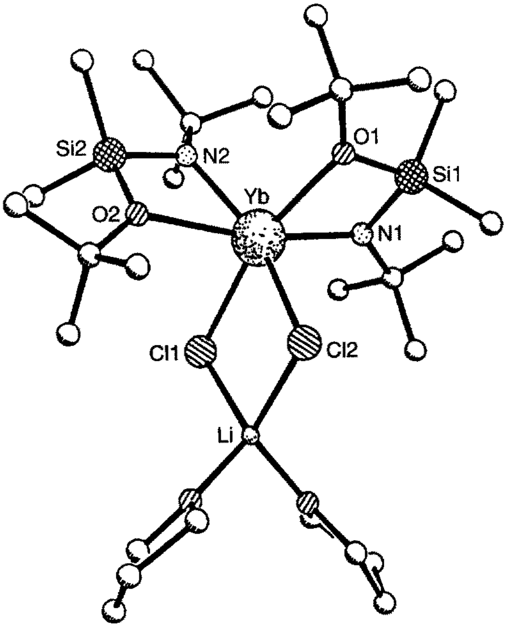


Fig. 21. Molecular structure of $[Me_2Si(OtBu)(NtBu)]_2Yb(\mu\text{-}Cl)Li(THF)_2$ **(66o)**

More recently this chemistry has been successfully extended to disubstituted yttrium derivatives [27]. The THF adduct of yttrium trichloride reacts with two equivalents of Li[$Me_2Si(OtBu)(NtBu)$] (**11**) to afford the ate-complex **67b**, which can be transformed into the THF solvate **68b** by treatment with pentane under reflux conditions (Scheme 7).

The chloro complex **68b** served as a useful starting material for the preparation of a variety of derivatives containing the $[Me_2Si(OtBu)(NtBu)]_2Y$ unit [27]. Typical reactions are summarized in Scheme 8.

A low-temperature X-ray diffraction study has been carried out on the monomeric bis(trimethylsilyl)methyl derivative $[Me_2Si(OtBu)(NtBu)]_2YCH(SiMe_3)_2$ (**69b**) (Fig. 22) [27]. The coordination geometry around the central yttrium atom can be described as distorted trigonal-bipyramidal with two

$YCl_3(THF)_{3.5} + 2Li[Me_2Si(OtBu)(NtBu)]$

11

$\xrightarrow[-\text{LiCl}]{\text{THF}} [Me_2Si(OtBu)(NtBu)]_2Y(\mu\text{-}Cl)_2Li(THF)_2$

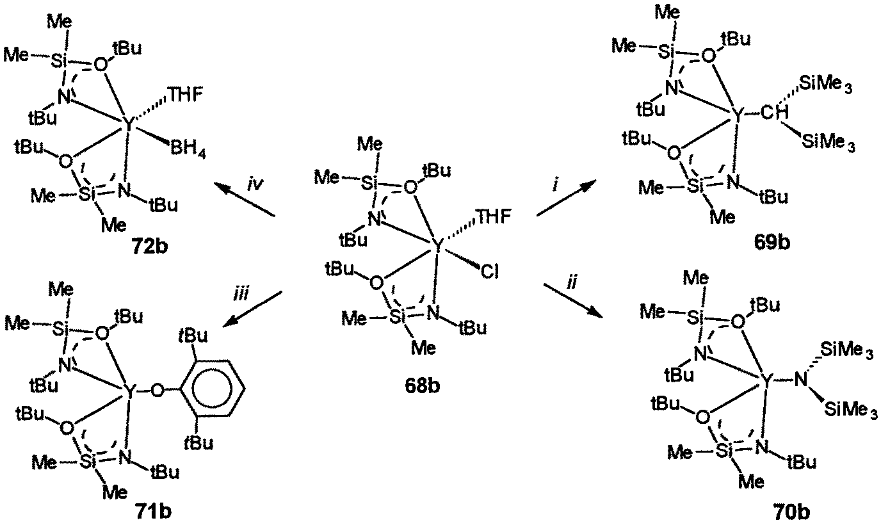
67b

$\downarrow$

$[Me_2Si(OtBu)(NtBu)]_2YCl(THF)$

68b

Scheme 7. Preparation of $[Me_2Si(OtBu)(NtBu)]_2YCl(THF)$ (**68b**)



Scheme 8. Preparation of $[Me_2Si(OtBu)(NtBu)]_2Y$ derivatives (*i*) $LiCH(SiMe_3)_2$, toluene; (*ii*) $NaN(SiMe_3)_2$, toluene; (*iii*) LiO-2,6-$tBu_2C_6H_3$, toluene; (*iv*) $LiBH_4$, ether.

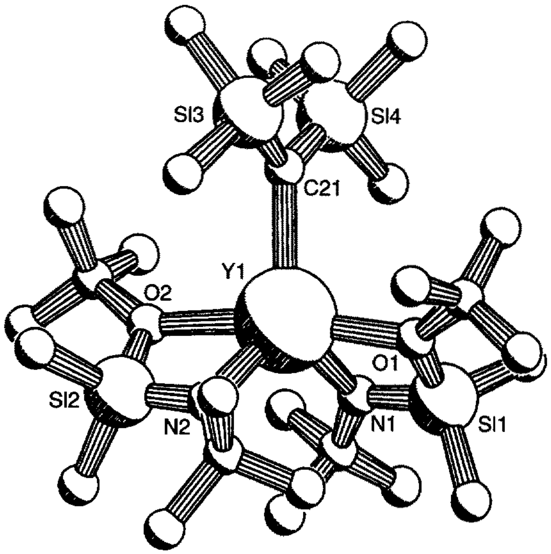


Fig. 22. Molecular structure of $[Me_2Si(OtBu)(NtBu)]_2YCH(SiMe_3)_2$ (**69b**)

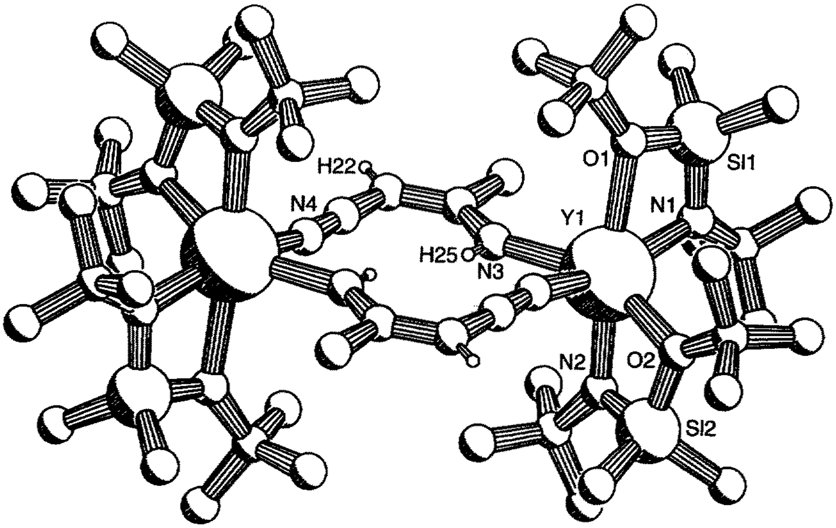
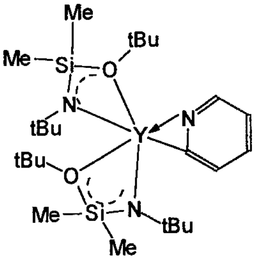


Fig. 23. Molecular structure of $[\{Me_2Si(OtBu)(NtBu)\}_2Y\{\mu\text{-}(N,N')\text{-}N(H)C(Me){=}C(H)C{\equiv}N\}]_2$ (**73b**)

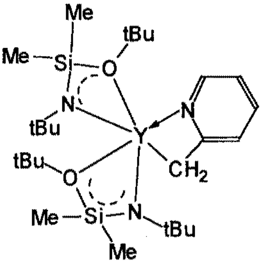
chelating alkoxysilylamide ligands and one σ-alkyl group attached to the metal. As observed for other structurally characterized lanthanide bis(trimethylsilyl)methy complexes, the α-carbon atom is planar.

The σ-alkyl complex $[Me_2Si(OtBu)(NtBu)]_2YCH(SiMe_3)_2$ (**69b**) is highly reactive and undergoes protolytic reactions with various reagents as well as hydrogenolysis with molecular hydrogen. Treatment with acetonitrile results in dimerization of the nitrile and formation of a dimeric species containing bridging crotonitrileamido ligands. Figure 23 shows the molecular structure of $[\{Me_2Si(OtBu)(NtBu)\}_2Y\{\mu\text{-}(N,N')\text{-}N(H)C(Me){=}C(H)C{\equiv}N\}]_2$ (**73b**) [27].

Yet another interesting reactivity pattern of $[Me_2Si(OtBu)(NtBu)]_2Y\text{-}CH(SiMe_3)_2$ (**69b**) is the activation of C–H bonds in activated arene complexes upon treatment with pyridine derivatives. The reaction with unsubstituted pyridine gave low yields of the η^2-pyridyl complex **74b**, while the analogous reaction with α-picoline selectively produced the α-metalated product **75b**. Alternatively the same materials are also available via metathetical reactions of the chloride precursor $[Me_2Si(OtBu)(NtBu)]_2YCl(THF)$ (**68b**) with the corresponding lithiated pyridine derivatives. The molecular structure of the α-picolyl complex **75b** was determined by a single-crystal X-ray analysis (Fig. 24) [27].



74b



75b

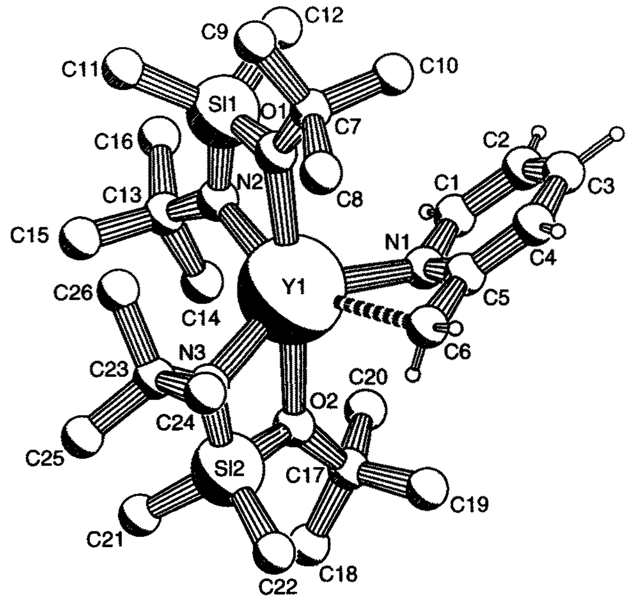


Fig. 24. Molecular structure of $[Me_2Si(OtBu)(NtBu)]_2Y(\eta^2\text{-}(C,N)\text{-}CH_2\text{-}2\text{-}NC_5H_4)$ (**75b**)

3 Conclusions

Bulky heteroallylic ligands have been demonstrated to be highly versatile observer ligands for lanthanide elements in their di- and trivalent oxidation states. Surprising parallels between the lanthanide complexes with heteroallylic ligands and the corresponding cyclopentadienyl complexes have been discovered. Several important advantages make these ligands systems very promising alternatives to the well-known cyclopentadienyl ligands. Initial investigations have shown that lanthanide complexes with heteroallylic ligands may be very useful as precursors for lanthanide-based materials as well as homogeneous catalysts.

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Routes to Monomeric Lanthanide Alkoxides

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The following contribution deals with lanthanide alkoxide chemistry under the aspects of "organic ligand synthesis – metal complexation – application". Special emphasis is put on the design and synthesis of tailor-made ligand environments. In particular, the methodology of donor-functionalization opens the way to creating several intriguing properties simultaneously – prerequisites for potential applications as highly selective catalysts for organic synthesis and precursors to ceramic materials. Detailed structural information on such tailored metal complexes, which is now available, provides the basics to understanding and optimizing the pursued applications. Concrete examples document the unique breaking and generation of lanthanide alkoxide bonds under thermal stress as well as under catalytic and related reaction conditions. The literature is covered until mid-1995.

List of Symbols and Abbreviations

al	aliphatic
Am	amyl
Ar	Aryl
BINOL	binaphthol
cat	catecholate
CN	coordination number
CH	hydrocarbon-based
CHF	fluorinated hydrocarbon
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
DHPEX	α,α'-di[(*S*)-2-hydroxy-2-phenylethyl]-*o*-xylenedioxide

diglyme	di-β-methoxyethylether
ditox	di-*tert*-butyl methoxide
DME	1,2-dimethoxyethane
do	donor-functionalized
Hbdmap	1,3-bis(dimethylamino)propan-2-ol
Hbdmmp	2,6-bis[(dimethylamino)methyl]-4-methylphenol
H_3(1,2,4-btt)	N, N', N'''-tris(2-hydroxybenzyl)triethylenetetramine
hfa	hexafluoroacetate
hfacac	1,1,1,5,5,5-hexafluoroacetylacetonate
hftb	2,2,2,4,4,4-hexafluor-*tert*-butanol
HMPA	hexamethylphosphoramide
H_3trac	tris[(4-hydroxypentenylidene-2-imino)ethyl]amine
Ind	indenyl
L	ligand
Ln	lanthanide (Sc, Y, La, Ce-Lu)
meditox	di-*tert*-butylmethyl methoxide
pftb	perfluor-*tert*-butanol
pip	piperidine
proditox	di-*tert*-butylisopropyl methoxide
silox	tri-*tert*-butyl siloxide
sipox	tri-isopropyl siloxide
TBHP	*tert*-butylhydroperoxide
tea	triethanolamine
thd	2,2,6,6-tetramethyl-3,5-heptanedionate
THF	tetrahydrofurane
TMEDA	tetramethylethylenediamine
tritox	tri-*tert*-butyl methoxide
trop	tropolonate
tripox	tri-isopropyl methoxide

1 Introduction

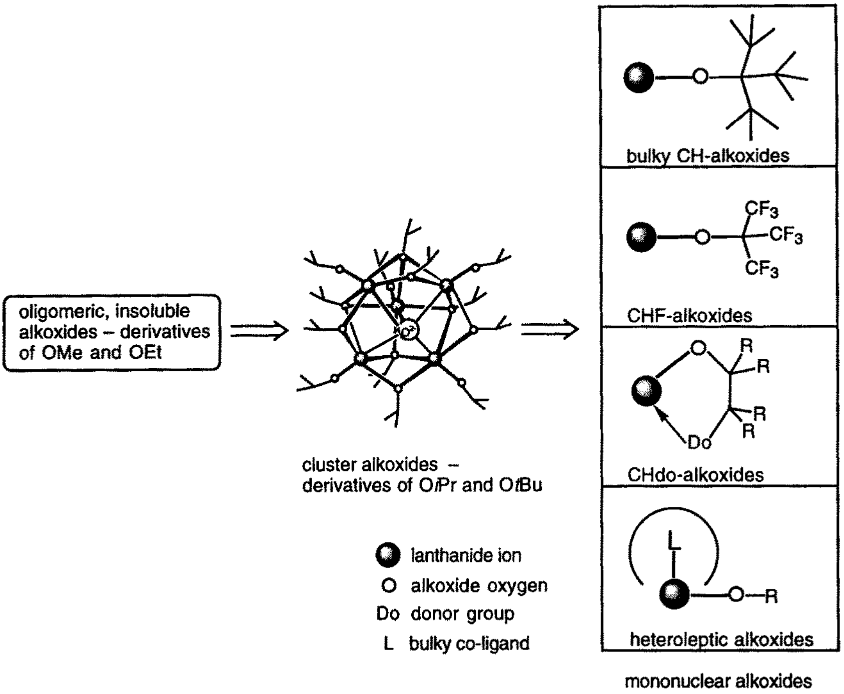
Routes to "monomeric", "mononuclear", "monolanthanide" alkoxides, enolates, siloxides and aryloxides – an expanded title which will put the scope of the article in a more concrete form. The synthesis of mononuclear alkoxides, in particularly homoleptic derivatives [1], was decisively stimulated by the discovery of high temperature superconducting ceramics based on $YBa_2Cu_3O_{7-\delta}$, where yttrium represents the lanthanide elements [2]. The support of volatile and highly soluble molecular precursors is a prerequisite for synthesizing thin films of these materials by means of MOCVD [3] and sol gel processes [4], respectively. More recently, lanthanide alkoxide reagents became established in organic synthesis [5]. Again, the use of well-defined, mononuclear precatalysts and catalytically active species facilitates the elucidation and optimization of the envisaged process. The comparatively kinetic lability of the Ln-O(R) bond turns out to be advantageous in these catalytic transformations.

Besides the promising options of applications, the enterprize "monomeric lanthanide alkoxides" bears a special challenge for the synthetic chemist due to the intrinsic properties both of the lanthanide cations [6] and the alkoxide ligand [7]. Several routes have been developed to meet this topic (Scheme 1). A major drawback regarding this goal is the usually observed oligomerization which occurs when the "large" oxophilic lanthanide metals are exposed to commmercially available alcohols. These alkoxide ligands tend to act as bridging ligands (Fig. 1) and the degree of agglomerization is dependent on the steric bulk of the OR-ligand. However, the electronic situation of the ligand also affects the extent of oligomerization. Figure 1 catches up this point by ordering various relevant ligands according their increasing pK_a values [8], which are generally directly proportional to the bridging tendency and instability against hydrolysis of the corresponding alkoxide complexes.

Lanthanide alkoxides derived from the less bulky alcohols, methanol or ethanol, are described as oligomeric, insoluble materials [7] whose exact structures have never been determined. Bulkier alkoxide ligands such as O*i*Pr [9] and O*t*Bu [10] generate pentanuclear and trinuclear species, respectively. Depending on the method of preparation, additional counter ligands are incorporated [11]. The presence of radially shaped charge densities as represented by O^{2-}, OH^- or Cl^- guarantees high coordination numbers for the metal in combination with high agglomerization states. Clusters thus formed are generally robust and are often thought of as transitions to solid oxide materials (Scheme 1).

However, only the use of tailor-made ligands can ensure rigidity combined with mononuclearity and neutrality in chemical reactions. Such intrinsic properties have previously been particularly associated with the predominating cyclopentadienyl ligand [12]. The integration of ligand design and preparation as an essential synthetic tool is synonymous with marking a new epoch in alkoxide chemistry. The total blurring of the organic-organometallic chemistry boundary was impressively demonstrated by metal-salt mediated template synthesis of macrocylic alkoxide ligands [13], a class of compounds which is also considered in this article. Sections 2, 3, 4 and 5 will provide the "synthetic and structural" fundamentals of the different approaches towards mononuclearity outlined in Scheme 1 – guarantors for encouraging applications (Sect. 6).

Synthetic strategies to alkoxide complexes have been covered in full by previous reviews [14]. The silylamide route proved to be an advantageous method of preparation, especially in the case of homoleptic derivatives [15]. The group (IIIA) elements – scandium, yttrium and lanthanum – are considered as lanthanides on the basis of their general chemical similarity to the true lanthanides.



Scheme 1. Routes to monomeric lanthanide alkoxides

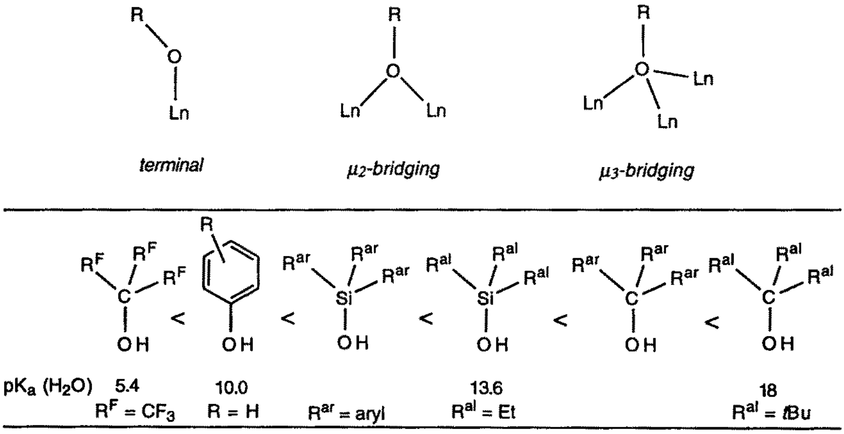


Fig. 1. OR-ligands: terminal and bridging bonding mode – depending on steric and electronic factors

2 Alkyl- and Phenyl-Substituted Ligands – CH-Alkoxides

Numerous commercially available primary, secondary and tertiary CH-alcohols have been used to synthesize alkoxide complexes of the type "Ln(OR)$_3$" and "Ce(OR)$_4$" (Scheme 2, [16]).

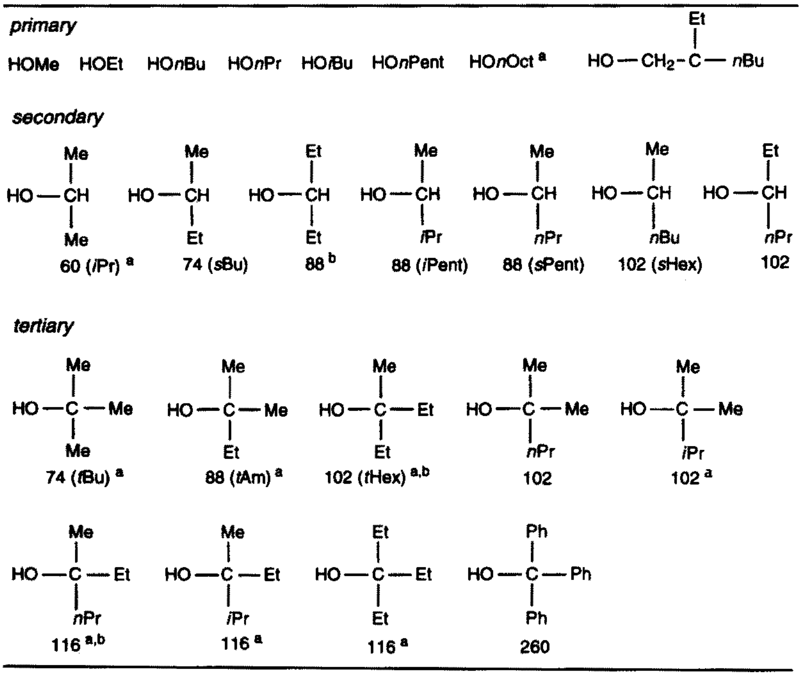
At the very beginning of these studies about 40 years ago, Bradley had already realized the influence of the steric bulk of the ligand on oligomerization and volatility of the resulting complex [17]. In 1978 the first structure determination of a CH-alkoxide revealed a hexanuclear arrangement in $Nd_6(OiPr)_{17}Cl$ [11]. Since then, halide "contamination" has often been observed when lanthanide halides were supported as precursors [18]. Scheme 3 represents structural trends in CH-alkoxide complexes depending on the steric bulk of the ligand. A promising candidate towards the putative mononuclear system was tri(*tert*-butyl)methanol, HOC*t*Bu$_3$ or H-tritox. This section will focus on utilization of this and slightly deviated ligands.

2.1 Ligand Synthesis

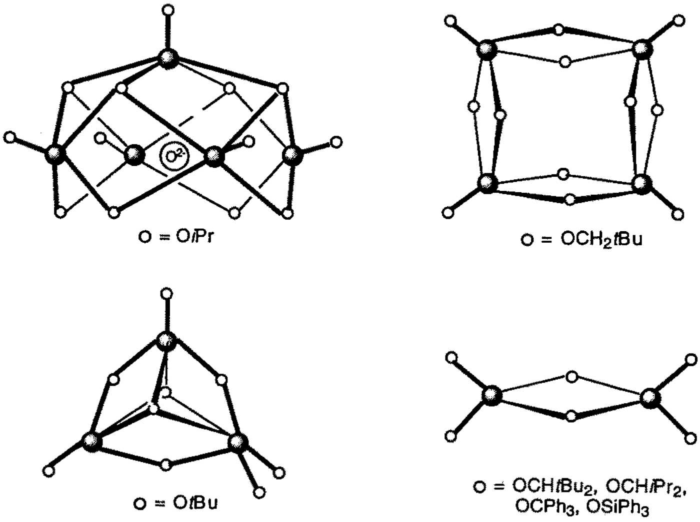
Bulky CH-alcohols can readily be synthesized according to standard organic procedures and are easily purified by distillation and sublimation, respectively (Scheme 4) [23–26].

Use of the tritox ligand was promising in so far as its steric requirements are usually discussed in comparison to those of the Cp ligand [27], which is capable of forming mononuclear complexes. In addition the tritox ligand is more flexible and, e.g., steric saturation can be achieved by agostic interactions [28]. A drawback of the tritox ligand is its thermal instability via release of isobutene and formation of the di(*tert*-butyl)methoxide ligand, ditox [29] (Sect. 6.3). Exchange of *tert*-butyl groups through isopropyl or even methyl groups in the tritox ligand will reduce the risk of β-alkene elimination. Hence the CH-alcohols H-proditox, H-meditox and H-tripox were synthesized with slight alterations of the steric bulk. In addition, lowering of the +I-effect of the alkyl groups would reduce the ease of formation of the tri-*tert*-butyl carbonium ion, which was associated with the heterolytic degradation of metal tritox complexes.

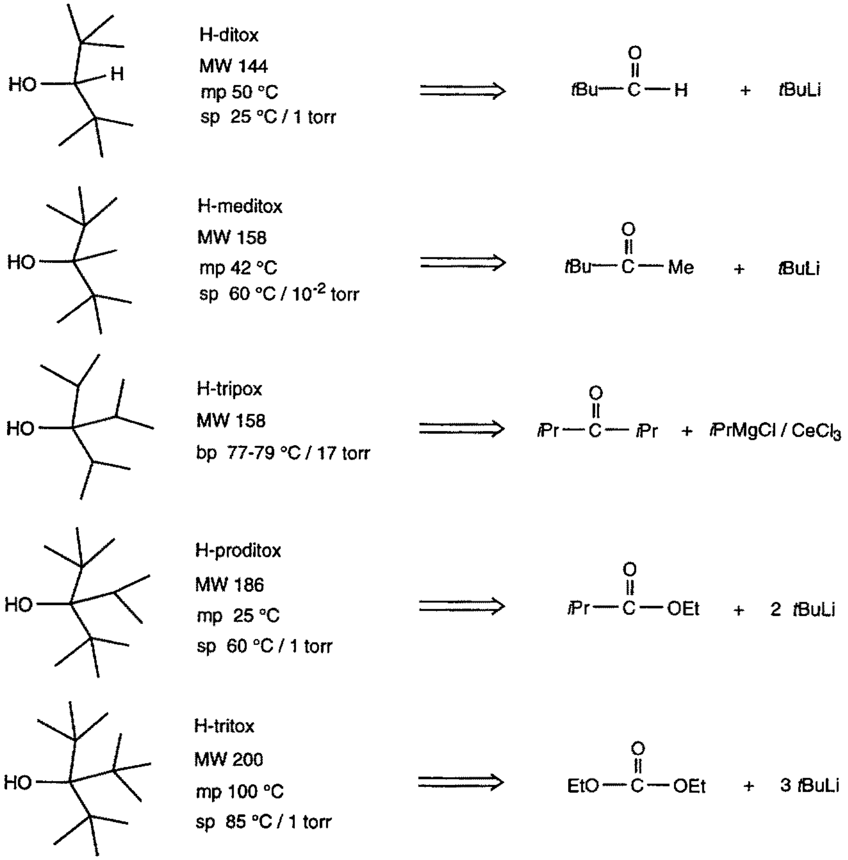
This decomposition pathway can also be affected by exchange of the C_α-atom through silicon. The strong silicon oxygen bond is kinetically stable with respect to heterolytic Si-O cleavage. In addition, the lower basicity of the siloxide ligands discourages the bridging tendency. Sterically hindered siloxide ligands have been reported in detail [30–33]. Scheme 5 shows both commercially available and synthesized siloxide ligands employed in lanthanide chemistry. Utilization of bulky H-silox [34] or H-sipox [35] compromises the previous arguments.



Scheme 2. Employed CH-alcohols listed according their molecular weight;
[a] sublimation behavior is described;
[b] Ce(IV) only



Scheme 3. Steric bulk of CH-alkoxide ligands OR and the degree of agglomerization (OR = O*i*Pr [9], O*t*Bu [10], OCH_2tBu [19], $OCHtBu_2$ [16], $OCHiPr_2$ [20], $OCPh_3$ [21], $OSiPh_3$ [22])

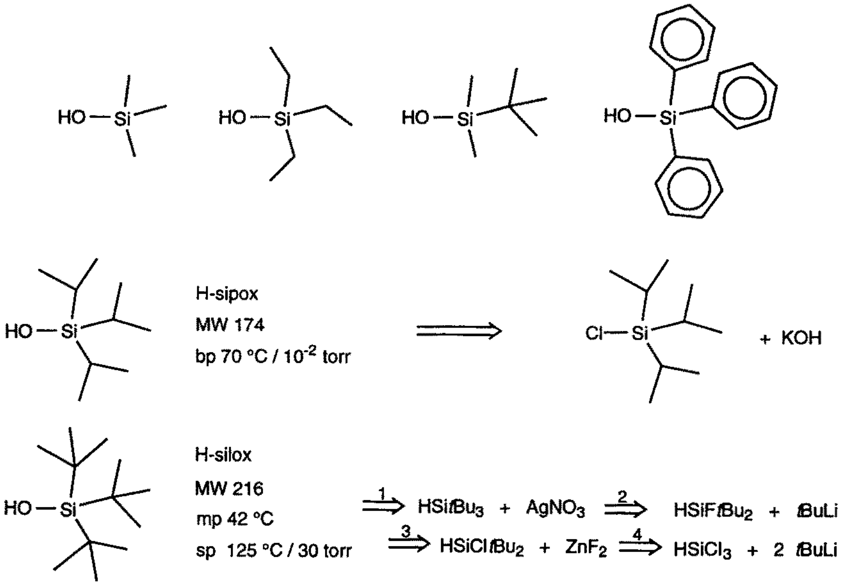


Scheme 4. Retrospective examination of bulky CH-alkoxides and their specification by molecular weight and boiling/sublimation point

2.2 Metal Complexes

2.2.1 Ln(III) Derivatives

Monomeric Ce(tritox)$_3$ was claimed in 1989 [29]. However, the structure determination was hampered by disordering problems both in solvent-free Ce(tritox)$_3$ and Nd(tritox)$_3$(THF) [36]. Appropriate crystallization conditions were borrowed from cyclopentadienyl chemistry. The corresponding LnCp$_3$ systems show remarkable crystallization behavior in the presence of neutral bases like acetonitrile and DMSO which impose polarities into the molecule [37]. Indeed, this phenomenon could be transferred to Nd(tritox)$_3$ in a 2-phase system *n*-pentane/acetonitrile at −35°C [38]. X-ray analysis revealed a monomeric alkoxide of formula Nd(tritox)$_3$(NCCH$_3$)$_2$ with a trigonal bipyramidal geometry at the neodymium center (Fig. 2, Table 1). The alkoxide O-atoms and



Scheme 5. Siloxide ligands employed in lanthanide chemistry

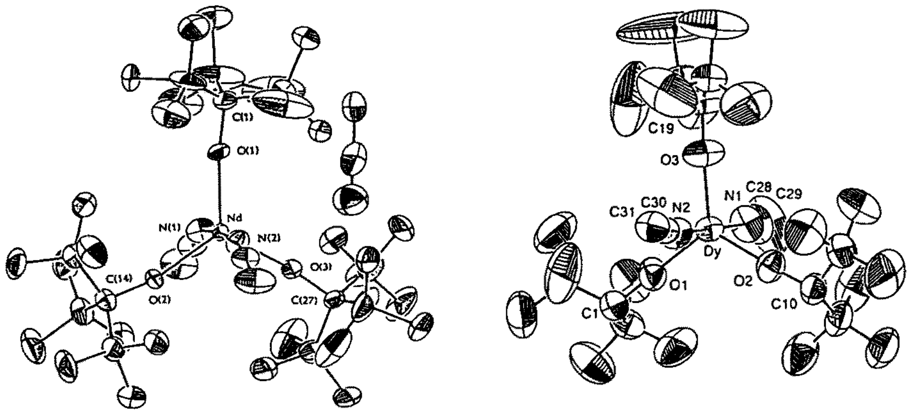


Fig. 2. Molecular structures of Nd(tritox)$_3$(NCCH$_3$)$_2$ [38] and Dy(ditox)$_3$(NCCH$_3$)$_2$ [39]

the neodymium atom lie in a plane while the two acetonitrile ligands occupy the apical vertices.

The molecular structure demonstrates the reduced steric requirement or enhanced steric flexibility of the tritox ligand compared to the Cp ligand. The bis(acetonitrile) adducts LnCp$_3$(NCCH$_3$)$_2$ can be crystallized only for Ln larger than neodymium.

The Ln(tritox)$_3$ system underlies a thermal degradation reaction (Sect. 6.3). Attempted sublimation yielded Ln(ditox)$_3$, the dimeric composition of which

Table 1. Lanthanide CH-alkoxides

Complex	Ln–O [Å]	Ref.
Nd(tritox)$_3$(NCCH$_3$)$_2$	2.149(5), 2.167(4), 2.171(5)	[38]
Nd(tritox)$_3$(THF)	2.150(3)–2.153(5)	[36]
[Tm(tritox)$_3$(μ-H$_2$NSiMe$_2$CH$_2$SiMe$_2$NH$_2$)]$_2$	2.021(4), 2.028(4), 2.044(3)	[40]
Dy(ditox)$_3$(NCCH$_3$)$_2$	2.057(5), 2.063(5), 2.064(5)	[39]
Nd(tritox)$_3$(μ-Cl)Li(THF)$_3$	2.150(3), 2.158(3), 2.171(3)	[42]
[Y(O*t*Bu)(Cl)(THF)$_5$][BPh$_4$]	2.026(4)	[45]
EuNa$_8$(O*t*Bu)$_{10}$Cl	terminal: 2.098(8)	[43]
YNa$_8$(O*t*Bu)$_{10}$Cl	terminal: 2.044(7)	[43]
YNa$_8$(O*t*Bu)$_{10}$(OH)	terminal: 2.02(2)	[43]
SmLi$_5$(O*t*Bu)$_8$	terminal: 2.135(7), 2.137(7)	[44]
[La(OSiPh$_3$)$_3$(THF)$_3$](THF)	2.228(6), 2.246(7), 2.303(4)	[47]
[Ce(OSiPh$_3$)$_3$(THF)$_3$](THF)	2.208(4), 2.224(4), 2.234(4)	[46]
[Y(OSiPh$_3$)$_3$(THF)$_3$](THF)	2.12(2), 2.14(2), 2.14(2)	[47]
Y(OSiPh$_3$)$_3$(OP*n*Bu$_3$)$_2$	2.121(3) 2.129(3), 2.118(3)	[47]
[Y(OSiPh$_3$)$_4$(η^2-DME)][K(η^2-DME)$_3$(η^1-DME)]	2.143(5), 2.147(5), 2.192(5), 2.196(5)	[47]
YCu(OSiPh$_3$)$_4$(PMe$_2$Ph)	2.071(3), 2.080(3), 2.154(3), 2.170(3)	[48]

was proven for the cerium derivative in the solid state [29]. The neodymium analogue retained the dinuclear constitution in the presence of coordinating solvents like acetonitrile, forming the asymmetric complex (ditox)$_2$Nd(μ-ditox)$_2$Nd(ditox)$_2$(NCCH$_3$) [39]. However, smaller lanthanide metals like dysprosium are capable of forming mononuclear adduct complexes under these conditions, as shown by Dy(ditox)$_3$(NCCH$_3$)$_2$ (Fig. 2, Table 1). The trigonal bipyramidal geometry is less distorted than in Nd(tritox)$_3$(NCCH$_3$)$_2$. The Dy-O-C angles are almost linear (about 177°). Alkyl fragments of one ditox ligand show, in part, enlarged thermal ellipsoids which are most likely due to disordering effects.

At this point the author would like to emphasize the importance and flexibility of the silylamide route. Ln(tritox)$_3$ complexes are readily available from Ln[N(SiMe$_3$)$_2$]$_3$ only for the larger lanthanide elements. However, the decreased steric bulk in Ln[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ amide precursors also allows the isolation of Ln(tritox)$_3$ complexes of the smaller lanthanide elements [16, 40].

Formation of a pseudomononuclear Tm(tritox)$_3$ has also been observed in a solid reaction between Tm[N(SiMe$_3$)$_2$]$_3$ and H-tritox at room temperature [40]. Under these conditions the amide/alcohol exchange is accompanied by an amide degradation. The formed silyldiamine is connecting two mononuclear Tm(tritox)$_3$ units in a dumb-bell fashion (Fig. 3, Table 1). The 4-coordinated thulium has a slightly distorted trigonal pyramidal ligand environment. The molecule shows a disordering due to a crystallographically imposed site symmetry (center of symmetry) as shown in Fig. 3. Interestingly, a pendant of this compound is again found in cyclopentadienyl chemistry, namley Cp$_3$Yb(NC$_4$H$_4$N)YbCp$_3$ with pyrazine as bridging moiety [41].

Fig. 3. Molecular structure of $(tritox)_3Tm(H_2NSiMe_2CH_2SiMeNH_2)Tm(tritox)_3$ along with the disordering model [40]

The existence of monomeric structures is also likely for systems derived from silox and proditox, which possess a similar steric bulk to tritox [16]. The mononuclear composition of $Nd(silox)_3$ is supported by the IR spectrum exhibiting only a few symmetric absorption bands [16]. The impact of the variation of the steric bulk of CH-alkoxides on thermal behavior is discussed in Sect. 6.3.

Ate complex $Nd(tritox)_3(\mu\text{-}Cl)Li(THF)_3$ was obtained during an attempted preparation of the *ate* complex $LiNd(tritox)_4$ starting from $NdCl_3$ and four equivalents of Li(tritox) (Fig. 4) [42]. In generally, such alkali metal chloride adducts are undesired reaction products in simple metathesis reactions. However, their formation turns out to be crucial in catalytic organic transformations (Sect. 6.2.1). The siloxy *ate* complex $[Nd\{N(SiMe_3)_2\}_3(OSiMe_3)][Li(THF)_4]$ is readily formed by addition of isolated $LiOSiMe_3$ to $Nd[N(SiMe_3)_2]_3$ (Nd-

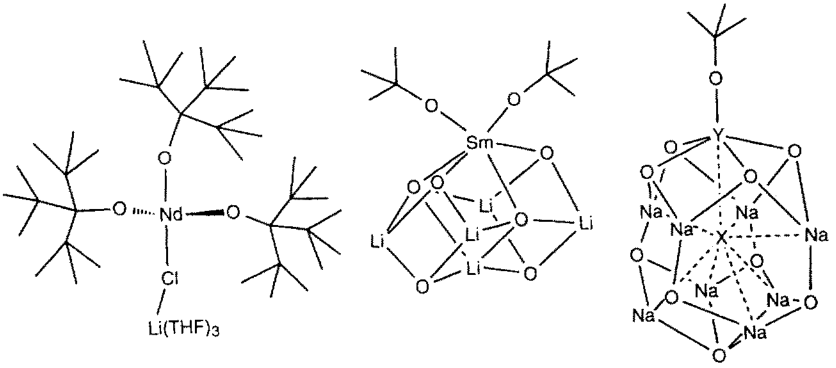
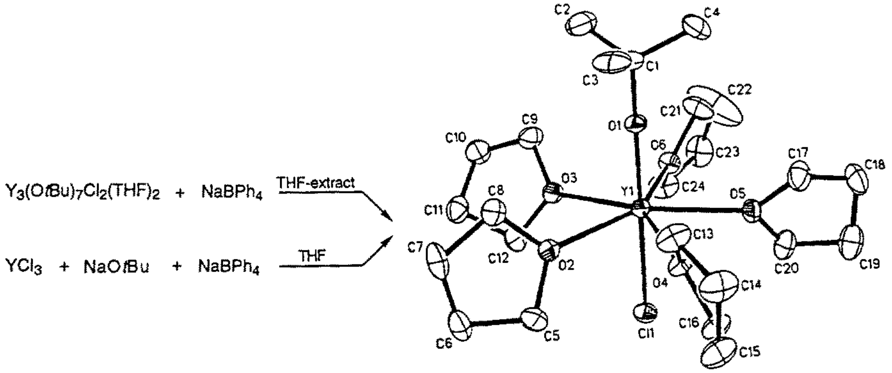


Fig. 4. *ate* Complex Nd(tritox)$_3$(μ-Cl)Li(THF)$_3$ (*left*) and LnM$_x$(O)$_y$ core of monolanthanide alkali metal clusters ("O" stands for bridging O*t*Bu ligands; terminal ones are depicted fully)



Scheme 6. Synthesis and molecular structure of cationic [Y(O*t*Bu)(Cl)(THF)$_5$][BPh$_4$] [45]

O = 2.17(1) Å). In both neodymium *ate* complexes the ligands adopt a distorted tetrahedral geometry around the metal center.

Monolanthanide complexes with high alkali metal content were obtained from reactions of LnCl$_3$ with excess (10 equiv.) of NaO*t*Bu [43]. The nonametallic complexes possess the general formula LnNa$_8$(O*t*Bu)$_{10}$X (Fig. 4, Table 1, X = Cl, OH). The main feature of the termial Ln-O-C fragments are again approximately linear bond angles (Ln-O-C [°]: Eu(Cl) 178.8(10); Y(Cl) 177.4(8); Y(OH) 176.3(21)). The related homoleptic complex SmLi$_5$(O*t*Bu)$_8$ was prepared by reacting [Li(tmeda)][Sm(CH$_3$)$_6$] with the alcohol [44]. The complex sublimes at 135°C/0.5 Torr. A SmLiO$_6$ core forms two face-linked cubes with samarium occupying a corner position. Two terminal *tert*-butoxy ligands complete its octahedral coodination (Fig. 4).

A remarkable cationic, highly solvated, heteroleptic monoyttrium complex [Y(O*t*Bu)(Cl(THF)$_5$][BPh$_4$] was obtained according Scheme 6 (Table 1) [45].

Despite ligation of typically bridging ligands, the cation adopts a mononuclear pentagonal bipyramidal geometry with the counterions in axial positions forming an almost linear arrangement of the Cl-Y-O-Cl moiety.

Use of less basic triphenylsiloxide ligands also allowed the isolation of mononuclear complexes (Table 1) [46, 47]. In addition to the silylamide route, anhydrous nitrates and isopropoxides were employed as synthetic precursors (Eqs. 1, 2). The siloxide bridges in the solvent-free dimeric systems $Ln_2(OSiPh_3)_6$ are readily disrupted by donor solvents like THF, $OPnBu_3$ or DME. The *tris*-THF adducts of lanthanum, cerium (Fig. 5) and yttrium adopt an approximately *fac*-octahedral geometry.

$$
\begin{aligned}
&(NH_4)_x\,Ln(NO_3)_{3+x} + (3+x)\ NaOSiPh_3(THF)\\
&\xrightarrow{THF} [Ln(OSiPh_3)_3(THF)_3](THF)\\
&\qquad + (3+x)\ NaNO_3 + x\ HOSiPh_3 + x\ NH_3 \qquad (1)
\end{aligned}
$$

$$
\begin{aligned}
&Y_5(OiPr)_{13}O + \text{excess}\ HOSiPh_3\\
&\xrightarrow{THF} [Y(OSiPh_3)_3(THF)_3](THF) + HOiPr \qquad (2)
\end{aligned}
$$

In $Y(OSiPh_3)_3(OPnBu_3)_2$ the oxygen-bond ligands roughly define a trigonal bipyramidal geometry with both phosphine oxides axial. The heterobimetallic complex $[Y(OSiPh_3)_4(\eta^2\text{-DME})][K(\eta^2\text{-DME})_3(\eta^1\text{-DME})]$ shows the yttrium metal in a pseudo octahedral oxygen environment [47].

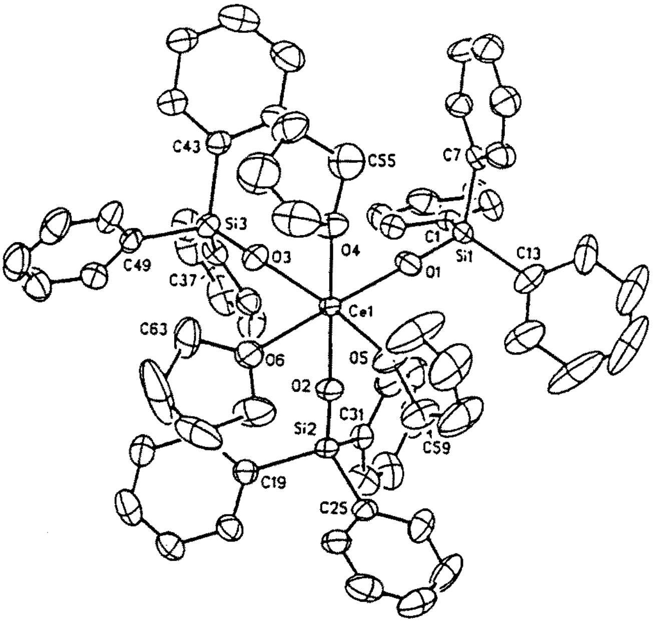
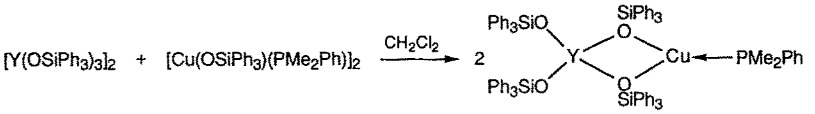


Fig. 5. Molecular structure of $[Ce(OSiPh_3)_3(THF)_3](THF)$ [46]

In contrast, $Nd_2(OCH\textit{i}Pr_2)_6$ cannot be deoligomerized by these solvents, including pyridine. This is in accord with the lower nucleophilicity of the siloxide O-atom which is reflected in the less distinct tendency to bridge the oxophilic lanthanide centers [20].

A mixed metal siloxide complex $YCu(OSiPh_3)_4(PMe_2Ph)$ was obtained by a simple addition reaction (Eq. 3) [48]. The geometry around the yttrium atom is distorted tetrahedral. The molecule is cleaved in solution by Lewis basic solvents like THF.



(3)

2.2.2 Ln(II) and Ce(IV) Derivatives

The effect of difference in both size and charge should favor the formation of monomeric Ce(IV) alkoxides rather than their trivalent analogues. Same arguments discourage the isolation of the corresponding Ln(II) systems. Ce(IV) is smaller than Ce(III) (0.87 vs 1.01 Å effective ionic radii for 6-coordination after Shannon [49]) and can accomodate four alkoxide ligands as counterions. Additionally, "hard" ligands like the alkoxide ligands should stabilize the high oxidation state Ce(IV) rather than Ln(II). Despite these encouraging prerequesites, Ce(IV) alkoxide chemistry suffers from synthetic problems [50]. For example, a convenient route comparable to the silylamide route has not yet been found. An alternative method of preparation utilizes cerium ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$, CAN) as starting compound [51]. Complexes with the less bulky O*i*Pr ligand already document the change in steric and electronic

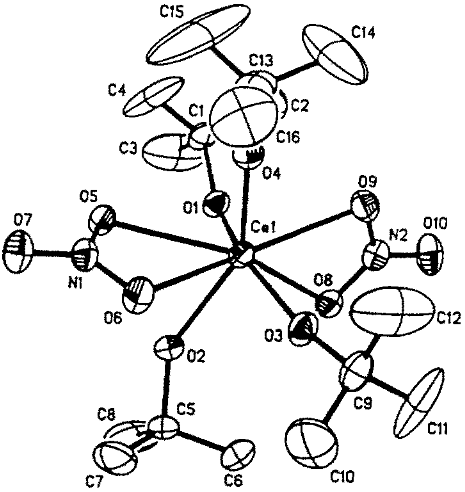


Fig. 6. Molecular structure of $Ce(O\textit{t}Bu)_2(NO_3)_2(HO\textit{t}Bu)_2$ [51]

requirements: dinuclear $Ce_2(OiPr)_8(HOiPr)_2$ [52] vs tetranuclear $Nd_4(OiPr)_{12}(HOiPr)_4)$ [9c]. Use of the O*t*Bu ligand even affords monomeric complexes as structurally evidenced by $Ce(OtBu)_2(NO_3)_2(HOtBu)_2$ (Fig. 6) and $Ce(OtBu)_4(\mu\text{-}OtBu)_2(\mu_3\text{-}OtBu)_2Na_2(DME)$ (Table 2) [51]. Stepwise exchange of the bidentate nitrate ligand through O*t*Bu ligands in the CAN/NaO*t*Bu system can be controlled by varying stoichiometry and the insolubility of $NaNO_3$ in THF (Eqs. 4 and 5). Homoleptic $Ce(OtBu)_4(THF)_2$ converts to $Ce_3(OtBu)_{10}O$ in toluene within a few days at room temperature.

A monomeric Ce(IV)-siloxide was prepared by an alcohol exchange reaction (Eq. 6). The 6-coordination in $Ce(OSiPh_3)_4(DME)$ is considered as a (4 + 2) environment with the four siloxy oxygen atoms occupying the sites of a distorted tetrahedron [53].

$$(NH_4)_2Ce(NO_3)_6 + x\ NaOtBu \xrightarrow[\substack{-2\ HOtBu \\ x=2-6}]{-2\ NH_3} Ce(OtBu)_{x-2}(NO_3)_{6-x}(THF)_2 + xNaNO_3 \tag{4}$$

$$(NH_4)_2Ce(NO_3)_6 + 8\ NaOtBu \xrightarrow[-2\ HOtBu]{-2\ NH_3} Ce(OtBu)_6Na_2(THF)_4 + 6\,NaNO_3 \tag{5}$$

$$\text{“}Ce(OiPr)_4\text{”} + 4\ HOSiPh_3 \longrightarrow Ce(OSiPh_3)_4 + 4\ HOiPr \tag{6}$$

The mixed alkoxide/aryloxide complex $(tritox)_3Ce(OC_6H_4O)Ce(tritox)_3$ was obtained by reaction of $Ce(tritox)_3$ with benzoquinone [54]. Its molecular arrangement resembles that in the pseudomononuclear thulium tritox complex discussed earlier.

Mononuclearity in Ln(II) CH-alkoxides has not yet been proven by X-ray crystallography [28, 55, 56]. The dimeric heteroleptic complex $\{Yb[N(SiMe_3)_2](\mu\text{-}tritox)\}_2$ established the alkoxide ligand as the bridging moiety [28]. Mono-europium(II) complexes with tri-*tert*-butoxygermanate-, -Stannate and -plumbate ligands were reported and $Eu[Sn(OtBu)_3]_2$ was characterized by X-ray structure analysis (Table 2) [55b]

Table 2. Ce(IV) and Eu(II) CH-alkoxides

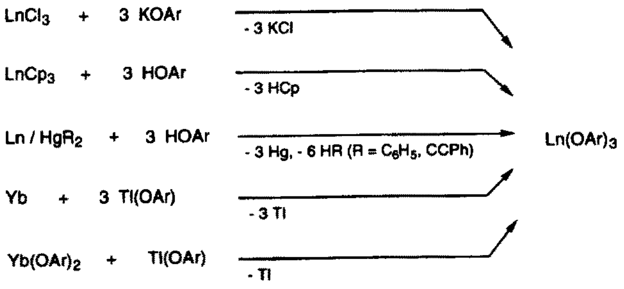
Complex	Ce–O [Å]	Ref.
$Ce(OSiPh_3)_4(DME)$	2.10(1), 2.10(1), 2.13(1), 2.13(1)	[53a]
$(tritox)_3Ce(OC_6H_4O)Ce(tritox)_3$	2.08(1), 2.09(1), 2.102(8) aryloxide: 2.09(1)	[54]
$Ce(OtBu)_2(NO_3)_2(HOtBu)_2$	2.023(5), 2.026(5)	[51]
$Ce(OtBu)_4(\mu\text{-}OtBu)_2(\mu_3\text{-}OtBu)_2Na_2(DME)$	terminal: 2.136(4), 2.146(4)	[51]
$Sn(\mu\text{-}OtBu)_3Eu(\mu\text{-}OtBu)_3Sn$	2.496(6)	[55b]

2.3 Aryloxide Complexes

Aryloxide-type complexes attracted attention as synthetic key precursors to lanthanide alkyls (Sect. 6.1) and as catalysts in organic synthesis (Sect. 6.2.1). They are generally of minor relevance in precursor chemistry of material sciences. Besides the silylamide route, various methods were developed to synthesize homoleptic complexes including halide metathesis reaction, protolytic ligand exchange and combined transmetallation/ligand exchange (Scheme 7). The $Ln(OAr)_3$ derivatives can be generated via sublimation in very pure and highly soluble form [57].

The use of unsubstituted or 4-methyl phenols resulted in the formation of cluster compounds [58]. However, 2,6-di(*tert*-butyl) substituted aryloxide ligands allowed the isolation of mononuclear "3-coordinate" homoleptic complexes of the lanthanide elements, the coordination mode of which was first demonstrated with the $N(SiMe_3)_2$ ligand [59]. The 2,6-substitution pattern is very effective because the alkyl groups are directed towards the metal center and impose a steric coordination number onto the metal which is comparable to the Cp* ligand (Cp*: 2.49; $OC_6H_3tBu_2$-2,6: 2.41) [60].

The mononuclear unsolvated constitution has been structurally defined for the early (Ce) [61] and late ("Sc", Y, Yb) elements (Table 3) [62,63]. The geometry of the Sc and Y derivatives is described as approximately trigonal planar with the metal center 0.13 and 0.09 Å, respectively, displaced from the O_3-plane. In contrast, the cerium derivative exhibits a pyramidal structure (Fig. 7). As in the $Ln[N(SiMe_3)_2]_3$ complexes, the cerium atom is disordered and



Scheme 7. Alternative routes to homoleptic aryloxide complexes

Table 3. Homoleptic lanthanide aryloxides

Complex	Ln–O [Å]	Ref.
$Sc(OC_6H_2Me\text{-}4\text{-}tBu_2\text{-}2,6)_3$	1.889(5), 1.854(5), 1.865(5)	[62]
$Y(OC_6H_3tBu_2\text{-}2,6)_3$	2.00(1), 2.00(2), 2.00(1)	[63]
$Ce(OC_6H_3tBu_2\text{-}2,6)_3$	2.140(5), 2.174(4), 2.135(5)	[61]
$Yb(OC_6H_3Ph_2\text{-}2,6)_3$	2.031(2), 2.061(4), 2.104(4)	[65a]

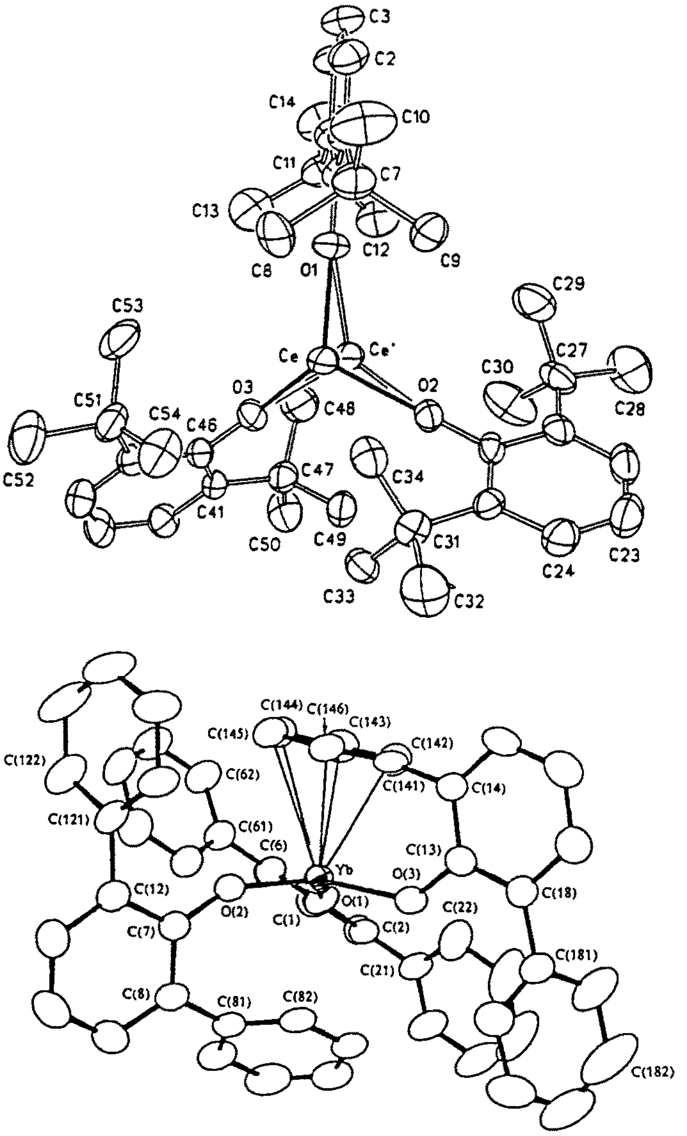


Fig. 7. Molecular structures of $Ce(OC_6H_3tBu_2\text{-}2,6)_3$ [61] and $Yb(OC_6H_3Ph_2\text{-}2,6)_3$ [65a]

occupies sites above and below the O_3-plane (0.54 Å). No additional γ-agostic contacts as in the thiolate analogue $Sm(SC_6H_2tBu_3\text{-}2,4,6)_3$ (Sm ··· C(Me) 3.02(3) Å) have been mentioned [64]. It is noteworthy that the "planar-pyramidal" problem has never attracted attention as in the $Ln[N(SiMe_3)_2]_3$ case.

The 2,6-diphenyl substituted aryloxide complex $Yb(OC_6H_3Ph_2\text{-}2,6)_3$ shows a similarly trigonal pyramidal LnO_3 skeleton with Yb 0.33 Å above the O_3-

plane (Fig. 7) [65a]. However, now the ytterbium is "frozen" in this position by significant Yb ··· π-arene interactions (average 2.978(6) Å) with the phenyl group tilted away from the O_3-plane by only 12.9 °. Another close Yb ··· C(Ph) contact of 2.882(5) Å on the opposite side completes the coordination sphere.

$Ln(OAr)_3$ systems readily form 5-coordinate adduct complexes in polar solvents (Table 4). $Ce(OC_6H_3tBu_2\text{-}2,6)_3(CNtBu)_2$ [61] and $La(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2$ [65b] exhibit a similar stereochemical arrangement. The adduct ligands occupy axial and equatorial positions of a distorted trigonal bipyramidal geometry. In contrast, the overall molecular structure in $Yb(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2$ consists of ytterbium coordinated in a square pyramidal fashion by two OAr and two THF ligands transoid at the basal sites and the Yb placed 0.57 Å towards an apical OAr ligand [65a]. The formation of mono adduct complexes of type $Ce(OC_6H_3tBu_2\text{-}2,6)_3(L)$ (L = THF, Ph_2CO, Et_3PO) was already detected in NMR spectral titrations [61] and could subsequently be established in the solid state. The 4-coordinated complexes $Yb(OC_6H_3tBu_3\text{-}2,4,6)_3(THF)$ [66] and $[Sm(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)](THF)$ [67] adopt a markedly distorted tetrahedral geometry with the ytterbium displaced only 0.392(1) Å from the O_3-plane. The ytterbium complex was prepared according Scheme 6 by redox transmetallation between ytterbium metal and the thallium(I)aryloxide or by oxidation of $Yb(OC_6H_3tBu_3\text{-}2,4,6)_2(THF)_3$ with the thallium reagent in tetrahydrofurane.

The sterically less demanding 2,6-di(isopropyl) aryloxide forms η^6-arene bridged dimers in the solid state which can be disrupted by THF [68]. Again, a distorted trigonal bipyramidal geometry is observed, although the THF ligands are now both placed in the axial positions. Also *ate* complexes of type $KLn(OC_6H_3iPr_2\text{-}2,6)_4$ have been isolated [69]. These complexes form infinite chain (Nd, Er) and sheet (La) structures by means of intra- and intermolecular K ··· arene interactions. The decreased bridging tendency of the aryloxide ligands compared to the CH-alkoxide ligands is further demonstrated by employing the 2,6-dimethyl substituted aryloxide [70]. Depending on solvent, both the dimeric and monomeric form could be isolated (Eq. 7). The mononuclear complex possesses the common coordination number six and contains a dis-

Table 4. Solvated lanthanide(III) aryloxides

Complex	Ln–O [Å]	Ref.
$[Sm(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)](THF)$	2.142(6), 2.148(7), 2.163(7)	[67]
$Yb(OC_6H_3tBu_3\text{-}2,4,6)_3(THF)$	1.97(1), 2.02(1), 2.09(1)	[66]
$Ce(OC_6H_3tBu_2\text{-}2,6)_3(CNtBu)_2$	2.239(5), 2.225(7), 2.231(7)	[61]
$[La(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2]$ (THF)	2.25(1), 2.25(1), 2.234(9)	[65b]
$Yb(OC_6H_3Ph_2\text{-}2,6)_3(THF)_2$	2.038(7), 2.111(9), 2.084(9)	[65a]
$Pr(OC_6H_3iPr_2\text{-}2,6)_3(THF)_2$	2.142(8), 2.158(9), 2.216(9)	[68]
$Gd(OC_6H_3iPr_2\text{-}2,6)_3(THF)_2$	2.138(9), 2.16(1), 2.096(9)	[68]
$Er(OC_6H_3iPr_2\text{-}2,6)_3(THF)_2$	2.07(1), 2.07(1), 2.09(1)	[68]
$Lu(OC_6H_3iPr_2\text{-}2,6)_3(THF)_2$	2.041(4), 2.048(4), 2.042(3)	[68]

torted *fac*-octahedral arrangement of ligands around yttrium.

$$[Y(\mu\text{-}OC_6H_3Me_2\text{-}2,6)(OC_6H_3Me_2\text{-}2,6)_2(THF)]_2 \underset{\text{toluene}}{\overset{\text{THF}}{\rightleftharpoons}} 2\ Y(OC_6H_3Me_2\text{-}2,6)_3(THF)_3 \qquad (7)$$

2.3.1. Ln(II) Aryloxide Complexes

Bulky aryloxide ligands also allowed the synthesis and characterization of divalent europium, samarium and ytterbium complexes. Homoleptic solvent-free complexes exist as aryloxide bridged dimers in the solid state [28]. However, uptake of two or three additional donating solvent molecules results in the formation of mononuclear complexes (Table 5). 4-coordinated complexes $Yb(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(L)_2$ ($L = THF$, OEt_2, hmpa) reveal a distorted tetrahedral geometry at ytterbium [71, 72]. Accommodation of three THF ligands produces a square pyramidal geometry at the metal center with two trans THF oxygens and trans aryloxide oxygen defining the basal plane [73]. The ytterbium is displaced 0.317(2) Å above the plane. The approach of a fourth THF ligand to generate an octahedral arrangement is sterically blocked by *tert*-butyl groups which form Yb ··· C(*t*Bu) contacts in the range of 3.424 and 3.94 Å, respectively.

Corresponding 5-coordinate samarium complexes can also be accomplished (Table 5) [74, 75] and heteroatom stabilization of the strongly reducing Sm(II) was observed in the *ate* complex $[KSm(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)]_n$ [75]. Indefinite chains or higher aggregations by K ··· arene interactions seems to be a common coordination mode in lanthanide aryloxide complexes.

3 Fluorinated Ligands – CHF-Alkoxides

The investigation of fluorinated alcohols as suitable ligands for low molecular lanthanide complexes was initiated in the early 1970s [76]. Recently, more detailed syntheses and characterization of derivatives of trivalent lanthanide

Table 5. Solvated lanthanide(II) aryloxides

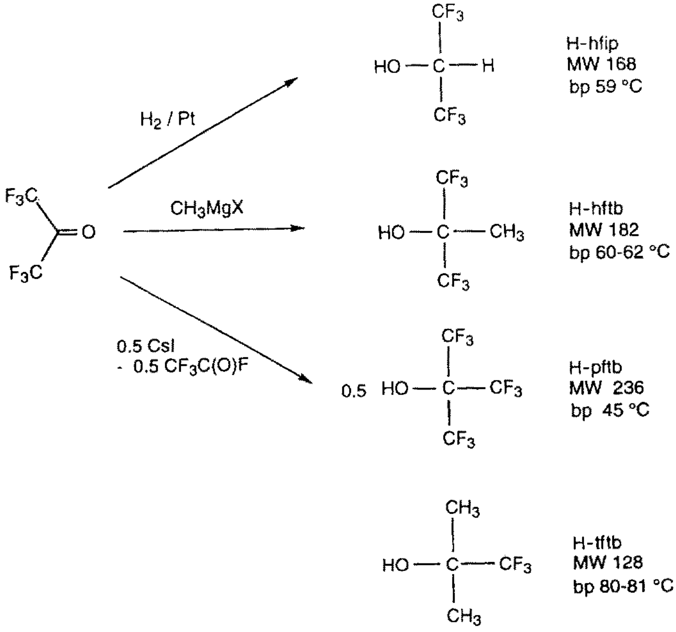
Complex	Ln–O [Å]	Ref.
$Yb(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_2$	2.135(9), 2.14(1)	[71]
$Yb(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(OEt_2)_2$	2.126(9), 2.182(8)	[71]
$Yb(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(hmpa)_2$	2.179(9)	[72]
$[Yb(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3](THF)_{0.5}$	2.20(2), 2.22(1)	[71]
$[Yb(OC_6H_3tBu_3\text{-}2,4,6)_2(THF)_3](THF)$	2.21(1), 2.22(1)	[73]
$[Sm(OC_6H_3tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3](THF)$	2.290(9), 2.318(7)	[74]

elements occurred [77–80]. These studies join the corresponding examinations involving other advanced ceramic relevant metals like copper [81, 82], barium [81], bismuth [83] and zirconium [84].

3.1 Ligand Specification

All fluorinated ligands depicted in Scheme 8 are commercially available. As shown in Scheme 8, a key precursor in the synthesis of these fluorinated alcohols is hexafluoroacetone HFA [85].

Fluorinated tertiary and highly fluorinated secondary alcohols are very stable. The exchange of CH_3 in CH-alkoxides by CF_3 groups results in a useful synergism with respect to oligomerization/volatility behavior. Increased intermolecular repulsions which commonly appear in fluorinated systems are already reflected in the boiling points of the employed alcohols ($HOC(CF_3)_3$: 45 °C, HO*t*Bu: 82 °C) and similarly affect the volatility of the resulting alkoxide complex. In addition to the significantly enlarged CF_3 groups compared to the CH_3 group, steric saturation of electrophilic metal centers can be accomplished by intramolecular close Ln ··· $F(CF_3)$ contacts. The electron withdrawing effect of the CF_3 group generates a less basic alkoxide O-atom compared to CH-alcohols and, as a result, a less distinct bridging tendency is observed. This combination renders a Ln-O bond of increased ionic character and hence an



Scheme 8. Synthesis and specification of fluorinated alcohols

electrophilic metal in a redoxstable environment. This metal-ligand constellation should also qualify for applications in catalyis as is already practiced with fluorinated β-diketonate complexes of the lanthanides [86]. Optically active CHF-alcohols have been reported [87].

3.2 Lanthanide CHF-Alkoxides

CHF-alkoxides were prepared from anhydrous $LnCl_3$ and alcohol in the presence of ammonia or according to the silylamide route. In both cases coordination of ammonia to the metal center could be observed. In the latter procedure ammonia is generated by excess of alcohol according to Eq. (8).

$$\begin{aligned}&Ln[N(SiMe_3)_2]_3 + \text{excess Hhftb}\\ &\xrightarrow[-2\,HN(SiMe_3)_2]{} [Ln(hftb)_3(NH_3)] + 2\,Me_3Si\text{-}hftb\end{aligned} \tag{8}$$

The solubility of unsolvated CHF-alkoxides in aliphatic and aromatic hydrocarbons is dependent on the number of ligand methyl groups and their degree of agglomerization was determined for trinuclear $[Pr(tftb)_3]_3$ [79]. However, the alkoxide bridges are readily disrupted in the presence of coordinating solvents like diethylether, THF, NH_3 or diglyme to yield dimeric and even monomeric complexes. $Ln(hftb)_3(THF)_3$ (Ln = La, Y) [78,80b] and $Y(hftb)_3(diglyme)$ [78] show 6-coordination, where two sets of ligands are disposed in a *fac*-octahedral configuration (Fig. 8, Table 6).

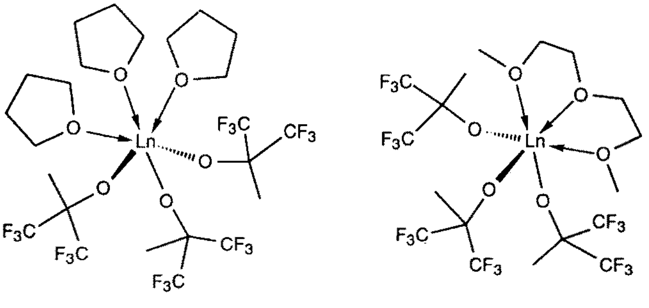


Fig. 8. *fac*-Octahedral configuration in solvated CHF-alkoxides

Table 6. Lanthanide CHF-alkoxides

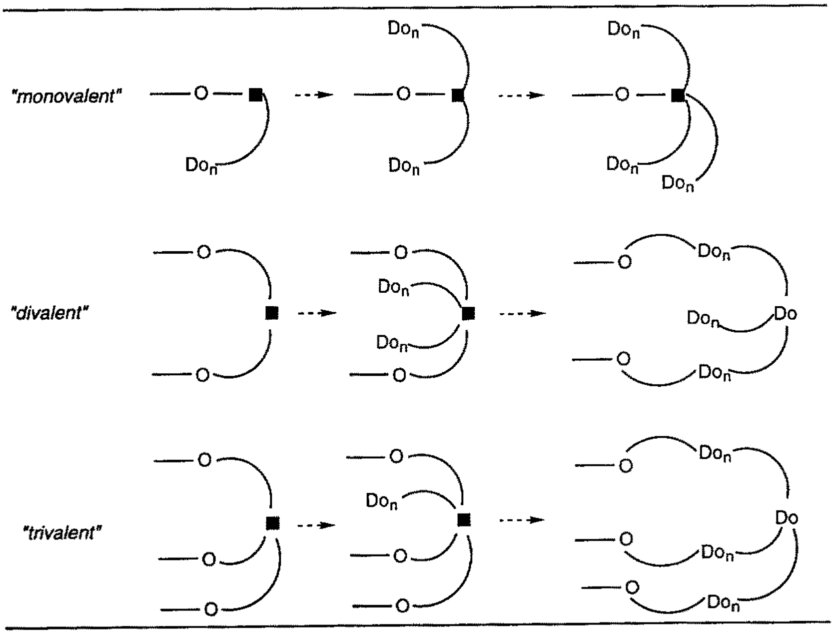
Complex	Ln–O [Å]	Ref.
$La(hftb)_3(THF)_3$	2.22(1), 2.23(1), 2.24(1)	[80b]
$Y(hftb)_3(THF)_3$	2.08(1), 2.09(1), 2.12(1)	[78]
$Y(hftb)_3(diglyme)$	2.06(2), 2.07(2), 2.08(2)	[78]

4 Donor-Functionalized Ligands – CHdo-Alkoxides

The foregoing two sections revealed that lanthanide centers like to expand their coordination sphere by additional adduct formation despite the presence of very bulky ligands such as tritox or $OC_6H_2tBu_3$-2,4,6. With regard to headwords such as "sublimation" and "homogeneity", these neutral co-ligands are a nuisance and undesired. For example, upon thermal treatment, they often separate off and dimerization occurs along with the formation of a less volatile species [29,78].

Internally tailoring of the alkoxide ligand with additional coordination sites leads to the class of functionalized ligands. When required, the alkoxide ligands can support these coordination sites using the effect of chelation. The idea donor functionalization of alkoxide ligands is developed in Scheme 9. Such modification of the tritox ligand as expressed in Fig. 9 represents a simple case of functionalization (monovalent, Do = OEt, n = 1).

"Do" stands for neutral donor sites like terminal -OR or -NR_2 and internal -O- or -NR- groups, respectively. However, multiply charged ligands like the doubly charged or "divalent" catechol and biphenol are also considered as functionalized ligands.



■ = center of branching

Scheme 9. Possible donor-functionalizations of alkoxide ligands

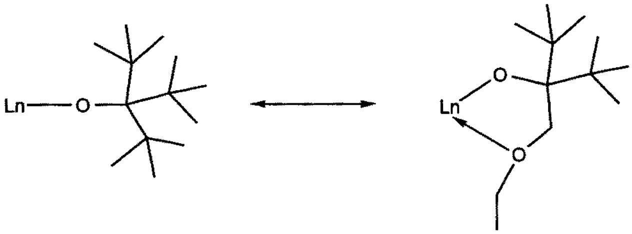


Fig. 9. Potentially monoclinching modification of the tritox ligand

The importance of the chelate effect combined with the construction of multidentate ligands is well known in lanthanide chemistry. This is expressed in the rich coordination chemistry of β-diketonates [88] or complexes with Schiff bases [89] and macrocyclic polyethers [90] where lanthanide cations achieve steric saturation by high coordination numbers. Entrapment of the cation in a macrocyclic cavity results in greater complex stability. However, simply functionalized ligands such as ethanolamines can also supply a suitable ligand sphere [91–93].

Detailed investigations of metal complexes of monovalent CHdo-alcohols were initiated to find alternatives to the β-diketonate complexes as precursors to ceramic materials. In particular, mononuclear and very volatile complexes of the elements Cu, Zn, Bi, Pb were pointing the way [94]. Section 4 will put the main emphasis on the adaptation of this strategy to lanthanide elements.

Another potential of functionalized alkoxide ligands was uncovered about ten years earlier. Tailor-made, predominantly multiply functionalized ligands attracted attention as models for binding sites of metallo-enzymes [95].

4.1 Monovalent Ligands

4.1.1 Monoclinching Alcohols

"Monoclinching" alcohols represent the simplest members of the monovalent family (Fig. 9). Several yttrium(III) and cerium(IV) complexes derived from simple aliphatic, monoclinching CHdo-alcohols are summarized in Table 7 [96–99]. The formation of a Ln-OCH_2CH_2OMe moiety was also observed during the reaction of $Ln[N(SiMe_3)_2]_3$ with $HSnEt_3$ by DME(solvent) cleavage [100].

Ligands with more rigid aromatic moieties afforded less soluble complexes (Fig. 10) [101–103]. For example, the rather inflexible tropolone produces neutral, high melting (ca. 400 °C) *tris*-tropolonates of extraordinary intractability [104]. Even in the presence of a solubilizing isopropyl group, derivatives of the larger elements remain insoluble in common solvents. The existence of polymeric lattices through bridging oxygen atoms was suggested.

However, despite poor solubility, the smaller scandium afforded discrete $Sc(trop)_3$ molecules in the solid state, demonstrating the efficiency of mono-

Table 7. Ln-complexes containing simple CHdo-alcohols

CHDo-alcohol	CHDo-alkoxide	Ref.
Yttrium(III)		
HOC_2H_4OMe	$[Y(OR)_3]_{10}$; $Y_3(\mu_3, \eta^2\text{-}OR)_2(\mu_2, \eta^2\text{-}OR)_2(\mu_2, \eta^1\text{-}OR)(acac)_4$	[96, 97a]
HOC_2H_4OiPr	$[Y(OC_2H_4OiPr)_3]_n$	[97b]
$HOC_2H_4NMe_2$	$[Y(OC_2H_4NMe_2)]_n$	[98]
Cerium (IV)		
$HOC_2H_4NEt_2$	$Ce(OR)(OiPr)_3$; $Ce(OR)_2(OiPr)_2$; $Ce(OR)_3(OiPr)$; $Ce(OR)_4$ $Ce(OR)_4(HOR)_2$; $Ce(OR)_4(HOR)_4$; $Ce(OR)_4(HOR)_5$	[99]

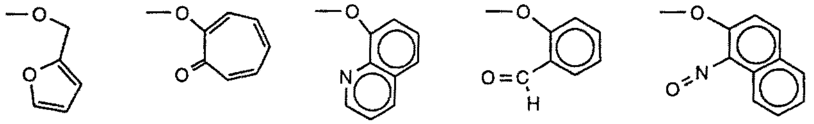

furfuralkoholato tropolonato 8-quinolato salicylaldehydato α-nitroso-β-naphtholato

Fig. 10. CHdo-alkoxide ligands with unsaturated moieties

clinching alcohols via chelate effect (Fig. 11, Table 8) [105a]. The complex could be purified by sublimation at 250 °C/0.1 Torr [105b]. Charge delocalization results in two equivalent enlarged Sc-O bond distances of 2.102(1) Å.

The isolation of mononuclear CHdo-alkoxides of the larger lanthanide elements requires steric bulk at the α-C-atom. In the absence of steric constraints the monoclinching alcohols tend to act as a bridging-chelating ligand rather than a chelating one, as it was shown, e.g., for the cyclic decamer $[Y(OCH_2CH_2OMe)_3]_{10}$ which contains μ_2:η^2-bridging ligands (Fig. 12, Table 7) [96].

Introduction of two methyl groups in α-position led to the formation of a dimeric $[Lu(OCMe_2CH_2OMe)_3]_2$ which contains a simply η^2-ligated ligand (Fig. 12) [106]. Another factor which influences or adds to the tendency of agglomerization is the presence of confined charge densities as oxo or hydroxy functionalities as evidenced in the tetrameric cluster $Lu(O)(OH)(OCMe_2CH_2OMe)_9$ [106]. The molecular structure exhibits three different bridging ligation modes, namely asymmetrically $\mu_3:\eta^2$, asymmetrically $\mu_2:\eta^2$ and symmetrically $\mu_2:\eta^1$.

Ligand Synthesis

Judging by their appearance, monoclinching alcohols resemble β-diketonate ligands (Fig. 13). Bulky (*t*Bu) or fluorinated (CF_3) alkyl groups in R^1 and R^3 position ensure volatility of β-diketonate complexes [107].

Therefore ligand synthesis has to put emphasis on both functionalization and steric bulk in α-position to meet the steric requirements of the lanthanide metals.

Table 8. CHdo-alkoxides with monoclinching ligands

Complex	Ln–O [Å]	β [°]	Ref.
Sc(troponolate)$_3$	2.102(1)	77.77(6)	[105a]
Nd(OC*t*Bu$_2$CH$_2$PMe$_2$)$_3$	2.174(2)	60.2(1)	[119]
Y(OC*t*Bu$_2$CH$_2$PMe$_2$)$_3$	2.090(4)	63.3(1)	[119]
Y[OSi*t*Bu$_2$(CH$_2$)$_3$NMe$_2$]$_3$	2.093(8), 2.098(5), 2.099(8)	87.0(3), 89.5(3)	[118]
Yb[OSi*t*Bu$_2$(CH$_2$)$_3$NMe$_2$]$_3$ [OSi*t*Bu$_2$(CH$_2$)$_3$NMe$_2$H]	2.062(6), 2.074(6), 2.077(6), 2.092(6)	–	[118]

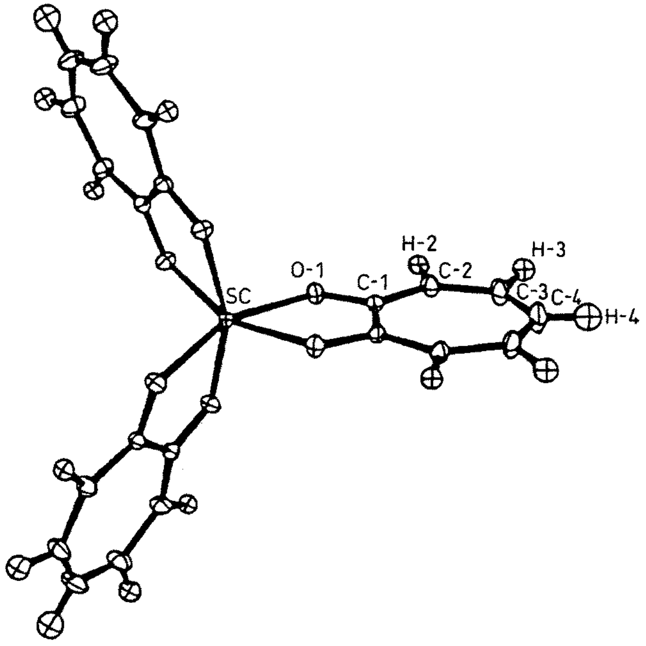


Fig. 11. Molecular structure of Sc(trop)$_3$ [105a]

The main feature of a chelating unit is its bite angle which can be expressed in figures of the angle O-Ln-Do "β" (used in this article) or the distance O-Do [108]. The synthetic tools allow a versatile ligand construction including tuning of solubility by variation of R, tuning of the size of the resulting metallacycle (5-, 6-, 7- ring) and tuning of the number of functionalities (next sections). Accompanying are tuning of the molecular mass and the incorporation of asymmetric carbon atoms. Introduction of both "hard" and "soft" Do sites is possible. Hard Do-functionalities should generate thermally stable Ln ··· Do contacts. The interplay between hard and soft may have an impact on the stabilization of the less common oxidation states II and IV and on the catalysis of organic transformations. The chelate effect (bite) should provide a favorable steric situation at the metal center.

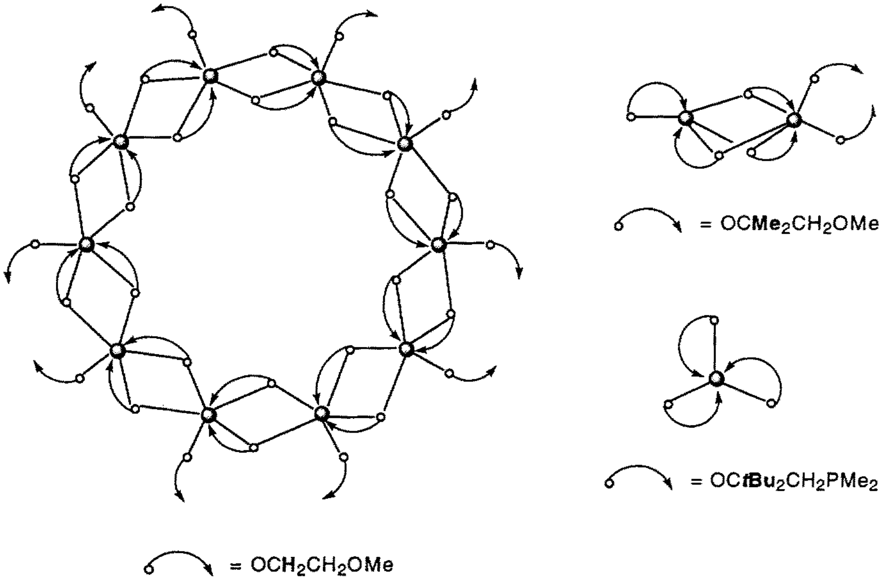


Fig. 12. The α-effect in complexes derived from monoclinching CHdo-alcohols

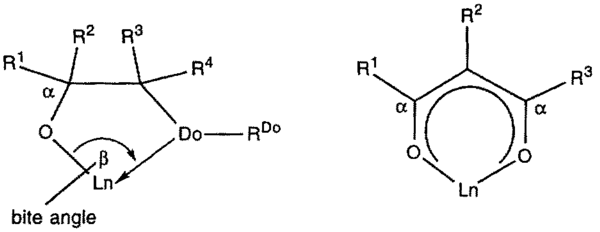
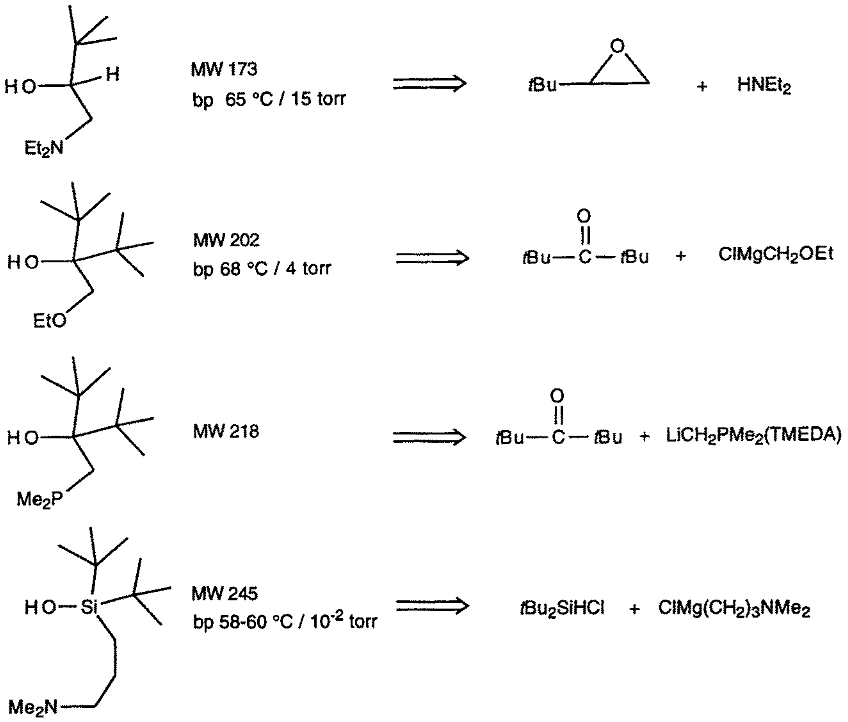


Fig. 13 Monoclinching CHdo-alcohols vs β-diketonates

In general, CHdo-alcohols can be prepared by standard organic procedures (Scheme 10), e.g., from appropriate nucleophilic reagents as lithium organyls, Grignard reagents, amines and carbonyl and epoxide precursors, respectively [109–117]. Steric congestion at the electrophilic center may cause prolonged reaction periods and lower yields [113]. Siloxides were synthesized from chlorosilanes and Grignard reagents and subsequent hydrolysis [118].

Monometallic Complexes

Isolation of the first examples of monomeric lanthanide alkoxides evidenced the importance of the "α-effect". Use of a highly hindered phosphino-alkoxide ligand afforded mononuclear, 6-coordinated $Ln(OCtBu_2CH_2PMe_2)_3$ (Ln = Y, Nd) with facial arrangement of the bidentate ligands (Fig. 14, Table 8). The



Scheme 10. Retrosynthetic examination and specification of several monoclinching CHdo-alcohols

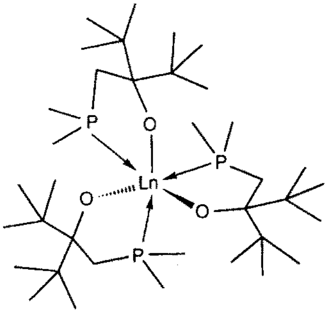


Fig. 14. Molecular drawing of $Ln(OCtBu_2CH_2PMe_2)_3$ [119]

$^{31}P\{^1H\}$ NMR spectrum of the yttrium derivative exhibited one of the first recorded couplings between ^{31}P and ^{89}Y ($^1J(^{31}P\text{–}^{89}Y) = 59$ Hz) [119].

Replacement of the soft PMe_2 donor group by hard NR_2 or OR groups ensured the isolation of thermally stable and sublimable derivatives (Sect. 6.3). However, high volatility and solubility went at the expense of poor crystallization behavior. At least their monomeric constitution could be not excluded from their mass spectra (Fig. 15) [120].

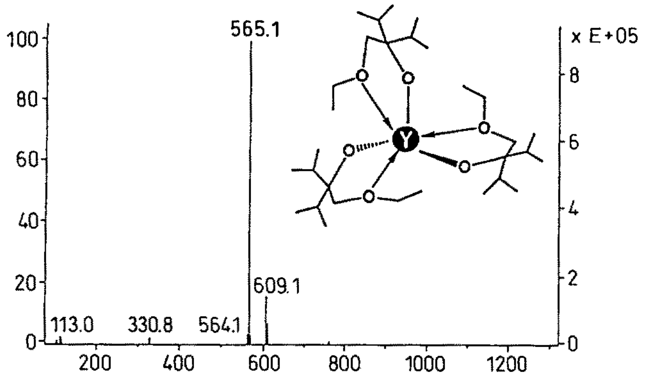


Fig. 15. FI-mass spectra of $Y(OC\textit{i}Pr_2CH_2OEt)_3$ [120]

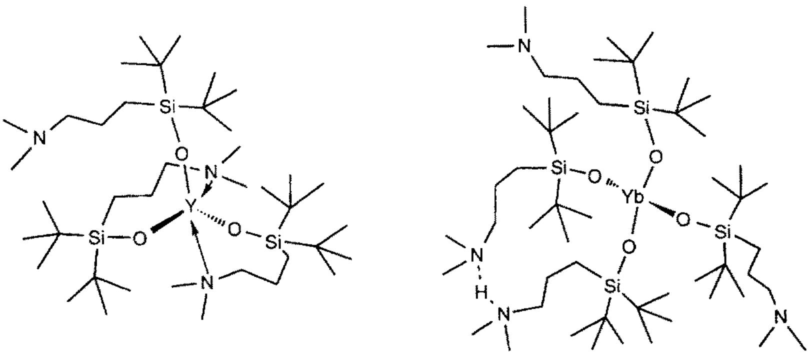


Fig. 16. Molecular drawings of $Y[OSi\textit{t}Bu_2(CH_2)_3NMe_2]_3$ (left) and $Yb[OSi\textit{t}Bu_2(CH_2)_3NMe_2]_3[OSi\textit{t}Bu_2(CH_2)_3NMe_2H]$ (right) [118]

A similar strategy was applied to synthesize monomeric siloxide complexes [118]. Only two of the siloxide ligands in $Y[OSi\textit{t}Bu_2(CH_2)_3NMe_2]_3$ form intramolecular Ln-NMe_2 contacts resulting in a trigonal bipyramidal geometry at the yttrium with the dimethylamino donors occupying the axial sites (Fig. 16, Table 8). The formation of a third 7-membered ring seems sterically unfavored. However, ^1H NMR studies support *mer*-octahedral geometry in the analogous complex containing the larger cerium. In the course of these studies it was shown that the internal dimethylamine groups can deprotonate a fourth equivalent of silanol to form a zwitter-ionic siloxide complex (Fig. 16, Table 8).

4.1.2 Double-, Triple- and Tetraclinching Alcohols

"Doubleclinching" alcohols are potentially tridentate ligands (two bite angles) and can be designed according to Fig. 17. They should be capable of stabilizing

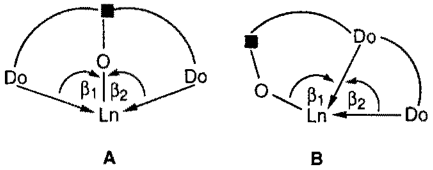


Fig. 17A, B. Choice of doubleclinching CHdo-alcohols (β_1, β_2: bite angles)

Ln(II) centers by a preferred 6-coordination in the presence of steric constraints. However, glancing at the related alkaline earth chemistry reveals that the formation of two neighbouring metallacycles with type **A** ligand underlies very sensitive steric restrictions [121]. Usually only one metallacycle is formed leaving the other Do group dangling or intermetallic-bridging. Alkaline earth complexes with β-diketonate ligands related to type **B** alkoxide afforded mononuclear complexes [122].

Homoleptic Ln(III) derivatives of doubleclinching alcohols will most likely produce dangling functionalities because 9-coordination will be less favored. Nevertheless, the first lanthanide(III) complexes derived from type **A** ligands exhibit promising reaction and coordination behavior. Complexes of type **B**, including $Y(OC_2H_4OC_2H_4OR)_3$ (R = Me, *n*Bu), show increased solubility in sol gel processes [123]. The molecular structure of $Ce_2(OiPr)_6(\mu\text{-}OC_2H_4NMeC_2H_4NMe_2)_2$ shows the aminofunctionalized ligand in the bridging position, whereas all isopropoxide groups are terminal [124].

Ligand synthesis

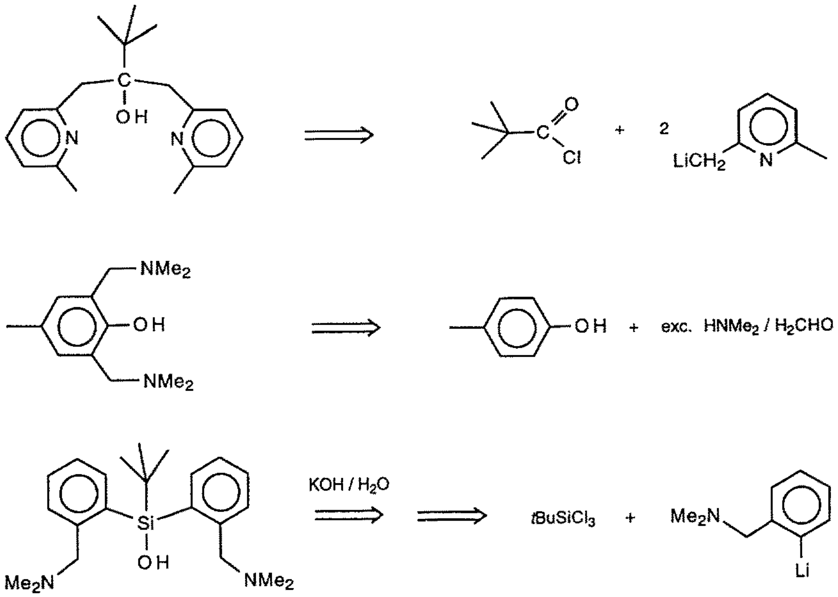
The methods of ligand preparation follow those of the corresponding monoclinching and divalent CHdo-alcohols [95, 125, 126]. Representative procedures are given in Scheme 11.

Monometallic Complexes

The homoleptic complex $Sm[OCtBu(2\text{-}CH_2\text{-}NC_5H_3\text{-}6\text{-}Me)_2]_3$ shows that none of the alkoxide ligands is attached to the metal in a tridentate fashion (Fig. 18, Table 9) [127]. Instead, two are bidentate and have trans oxygen and nitrogen donor atoms in the basal positions of a distorted square pyramid. The other alkoxide ligand is monodentate with its oxygen occupying the axial position and two uncomplexed nitrogen donor atoms oriented away from the metal with a Ln-N distances of > 5 Å. A total of four unattached lutidine groups surround the molecule and define an elongated tetrahedron which gives the molecule an outer shell of radially distributed unattached donor groups in addition to its inner coordination sphere.

Other homoleptic systems include the siloxide complex $Y\{OSitBu[(CH_2)_3NMe_2]_2\}_3$ [118].

The interplay of steric constraints and surplus Do functionalities create a ligand atmosphere which, for the first time, allowed the isolation of defined mixed ligand (amide/alkoxide) systems according the silylamide route. Both



Scheme 11. Retrosynthetic examination of doubleclinching alcohols [127–129]

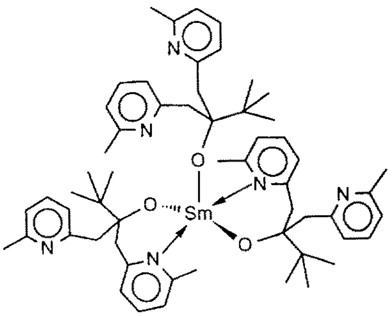


Fig. 18. Molecular drawing of Sm[OC*t*Bu(2-CH$_2$-NC$_5$H$_3$-6-Me)$_2$]$_3$ [127]

Table 9. Monovalent CHdo-alkoxides derived from higherclinching ligands

Complex	Ln–O [Å]	β [°]	Ref.
Sm[OC*t*Bu(2-CH$_2$-NC$_5$H$_3$-6-Me)$_2$]$_3$	2.116(2), 2.142(3), 2.172(3)	75.2(1), 75.6(1)	[127]
Yb[OC*t*Bu(2-CH$_2$-NC$_5$H$_3$-6-Me)$_2$]$_2$ [N(SiMe$_3$)$_2$]	2.057(4), 2.072(3)	78.2(2), 78.6(2)	[127]
Y[OSi*t*Bu(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$] = Y[OSi*t*Bu(C$_6$H$_4$-2-CH$_2$NMe$_2$)$_2$][N(SiMe$_3$)$_2$]$_2$	2.093(7)	82.7(3)	[128]
Pr[OC$_6$H$_2$(CH$_2$NMe$_2$)$_3$-2,4,6]$_3$(H$_2$O)$_2$	2.269(3), 2.280(3), 2.311(3)	70.0(1), 72.7(1)	[129]
LaL$_2$Cl(HL)[a]	2.342(6), 2.342(6)	68.8(2), 69.0(2)	[131]
PrL(NO$_3$)$_2$(HOCH$_3$)[b]	2.263(3)	69.9(1)	[132]

[a] L is shown in Eq. (9a), N-Pr-N [°]: 65.2(2), 66.1(2)

[b] L is shown in Eq. (9b), N-Pr-N [°]: 64.2(1), 65.3(1), 65.4(1)

monoamide and bisamide complexes have been structurally characterized (Fig. 19). The low temperature (– 40 °C) solution structure of $Y[OSitBu(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2][N(SiMe_3)_2]_2$ (^1H NMR) is consistent with the solid state molecular structure [128]. The yttrium center is 4-coordinate by one bidentate alkoxide and two silylamide ligands. Additionally a close Y ··· Si contact of 3.222(4) Å was observed. The two amide ligands could be replaced by 2,6-di-*tert*-butylphenol to yield a mixed alkoxide phenoxide complex.

A monoamide complex was obtained with $[OCtBu(2\text{-}CH_2\text{-}NC_5H_3\text{-}6\text{-}Me)_2]$ as a co-ligand (Fig. 19) [127]. The overall structure features are very similar to the aforementioned homoleptic Sm-system except that a monodentate alkoxide ligand has been replaced by a $N(SiMe_3)_2$ group. The amide group makes the complex soluble in aliphatic hydrocarbons.

A stabilizing option of the functionalized and highly hygroscopic ligand 2,4,6-tris(dimethylaminomethyl)phenol was demonstrated by the isolation of the remarkable water adduct complex $Pr[OC_6H_2(CH_2NMe_2)_3\text{-}2,4,6]_3(H_2O)_2$ according to the silylamide route [129].

Water coordination is commonly observed along with double charged homo- or heterofunctionalized complexes as catecholates (Sect. 4.2) and salicylates [130a], respectively. As in the case of fluorinated alkoxide complexes [130b], hydrolysis, which is rapid and complete for classic alkoxides yielding oxo and hydroxo derivatives, could be stopped at the first step. The molecular structure displays a 7-coordinate praseodymium center with one monodentate, two bidentate aryloxides and two water molecules adopting a distorted pentagonal bipyramid (Fig. 20, Table 9). The *cis*-positioned water molecules form short O ··· N contacts with dangling amino groups. One is involved in two intramolecular hydrogen bonds (O ··· N 2.794(5), 2.848(5) Å), while the other contacts one intramolecular (2.772(5) Å) and one intermolecular (2.810(5) Å) dangling amino group.

The lanthanum complex shown in Eq. (9a) is a rare example of a Schiff base derivative synthesized in nonaqueous solution [131]. 8-Coordination is accomplished by two tripleclinching aryloxide ligands, a phenolic contact of a free

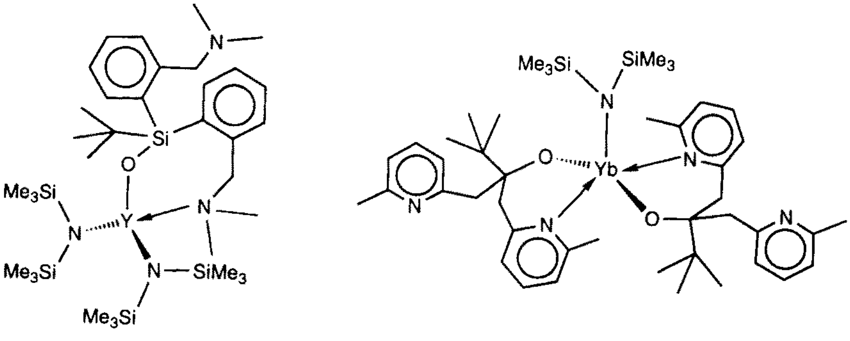


Fig. 19. Molecular drawings of $Y[OSitBu(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2][N(SiMe_3)_2]_2$ [128] and $Yb[OCtBu(2\text{-}CH_2\text{-}NC_5H_3\text{-}6\text{-}Me)_2]_2[N(SiMe_3)_2]$ [127]

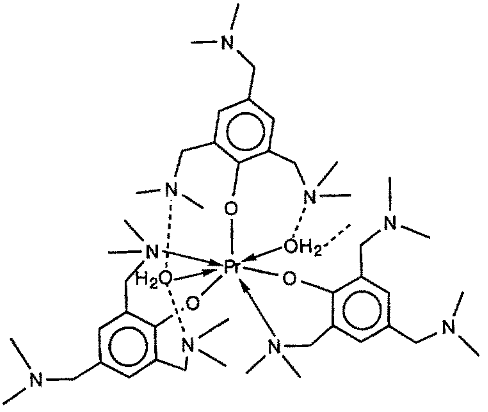
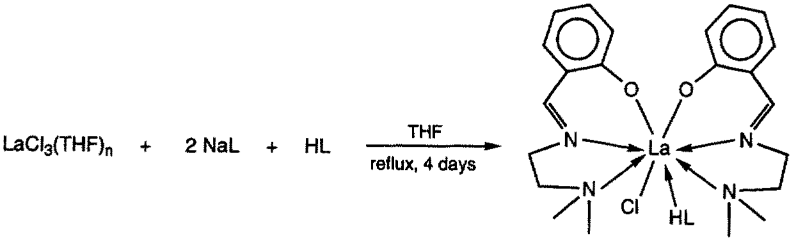


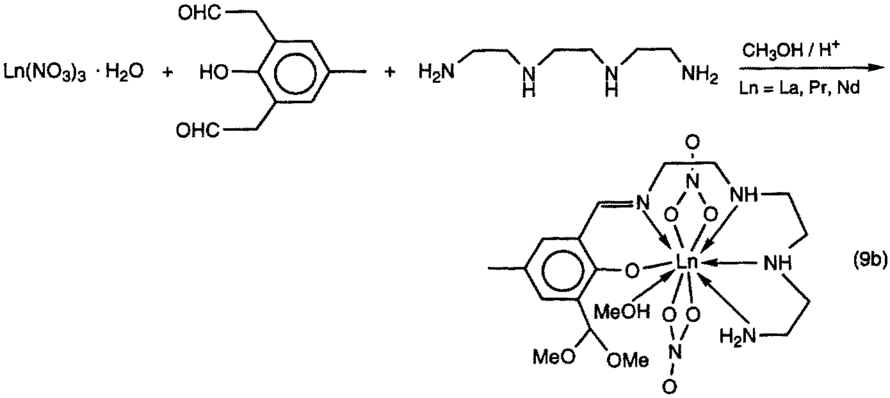
Fig. 20. Molecular drawing of Pr[OC$_6$H$_2$(CH$_2$NMe$_2$)$_3$-2,4,6]$_3$ (H$_2$O)$_2$ [129]

ligand and a chloride ligand (La-Cl 2.892(2) Å) susceptible to further functionalization.



(9a)

Acid catalyzed Schiff base condensation of 2,6-diformyl-*p*-cresol and TETA (triethylenetetraamine) with Pr^{3+} as the template cation (in methanol) afforded a 1 : 1 product containing a tetraclinching alcohol (Eq. 9b, Table 9) [132]. One of the carbonyl groups was acetylated under mild acidic conditions. The 10-coordination around Pr^{3+} achieved by one aryloxide site, one imine and three amino nitrogen, two bidentate nitrate anions and one molecule of methanol is best described as a bicapped square antiprism.

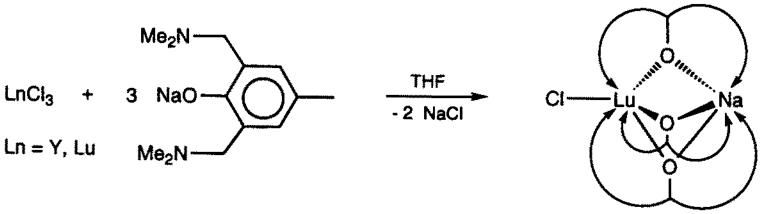


(9b)

4.1.3 Heterobimetallic Complexes

The tendency of CHdo-alcohols to act as bridging ligands, particularly in the absence of steric constraints (Scheme 12), is documented in the unintentional formation of homooligometallic systems such as $[\mathrm{Y(OCH_2CH_2OMe)_3}]_{10}$ [96] or $\mathrm{Ce_2(O}i\mathrm{Pr)_6(OC_2H_4NMeC_2H_4NMe_2)_2}$ [124]. However, this ligand option allows the strategic construction of heterobimetallic complexes (Table 10) for promising use as catalysts, single component precursors to ceramic materials and the study of magnetic and electronic interactions between d- and f-block elements on a molecular scale [13, 133]. Recently, systematic investigations were conducted to control and tune the complexation of mixed metal alkoxides which correspond to the first step in sol gel processing. Several review articles have been dedicated to this topic [4, 134]. The easy formation of mixed metal alkoxides illustrates the lability of the Ln-O(alkoxide) bond.

Cooperative anion-cation bonding is assumed to lead to the formation of the *ate* complex $\mathrm{Na\{Lu[OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4]_3Cl\}}$ (Eq. 10, Table 10) [135]. $\mu_2:\eta^3$-Bridging aryloxide ligands generate a "propeller-like" molecule with screw-type chirality. Asymmetric bonding of the phenolate ligands is observed both in the solid state and in solution. The sodium cation is accommodated in an $\mathrm{O_3N_3}$ pocket opposite to the chloride ligand. Examination of the crystal packing reveals a continuous $\{(\mathrm{Na}\cdots\mathrm{Lu\text{-}Cl})\cdots(\mathrm{Na}\cdots\mathrm{Lu\text{-}Cl})\}_n$ string through the crystal with inter- and intramolecular Na-Cl distances of 4.765(3) and 5.947(3) Å, respectively.



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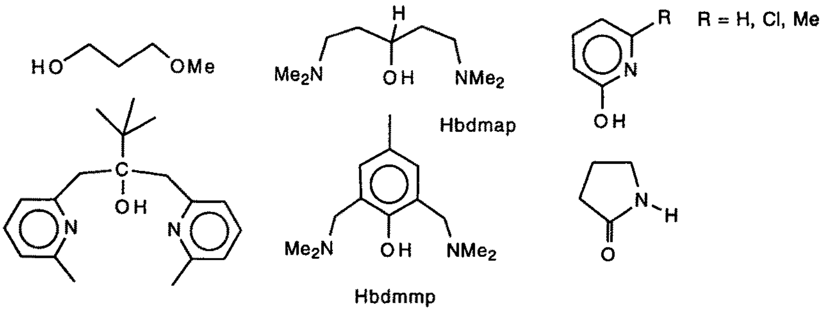


Scheme 12. CHdo-alcohols as assembling ligands in heterobimetallic complexes

Table 10. Heterobimetallic monolanthanide CHdo-alkoxide complexes

Complex	Ln–O [Å]	β [°]	Ref.
NaSm[OCtBu(2-CH$_2$-NC$_5$H$_3$-6-Me)$_2$]$_2$ [OC(CMe$_3$)=(2-CH-NC$_5$H$_3$-Me-6)]$_2$	2.394(4), 2.394(5) 2.215(5), 2.230(4)	70.5(2), 72.3(2)	[127]
Na{Lu[OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4]$_3$Cl}	2.143(3), 2.150(3), 2.174(3)	–	[135]
La(tea)$_2$[Nb(OiPr)$_4$]$_3$	av. 2.499(6)	65.4(2)	[136]
[(thd)$_4$YCu$_3$(OCH$_2$CH$_2$OMe)$_5$]	2.27(1), 2.294(7), 2.315(8), 2.425(8), 2.464(7)	65.2(3)	[137]
[(hfa)$_2$Y(thd)$_2$Cu$_2$(OCH$_2$CH$_2$OMe)$_3$]	2.218(5), 2.258(5), 2.505(6)	63.5(2), 63.8(2)	[137]
PrCu[bdmmp][Hbdmmp](μ-OH)(hfacac)$_3$	2.434(8)	–	[138]
LaCu$_2$(bdmap)$_3$(O$_2$CCF$_3$)$_4$	2.42(1), 2.84(2)		[139]
(HOMe)(NO$_3$)$_3$LaL$_5$Cu$_3$(OMe)(HOMe)[a]	2.366(3), 2.589(3), 2.630(3)		[141b]
(NO$_3$)$_3$LaL$_8$Cu$_3$(HOEt)[a]	2.358(7), 2.386(6), 2.402(5), 2.403(6), 2.570(5), 2.598(5)		[141b]

[a] L is shown in Scheme 14

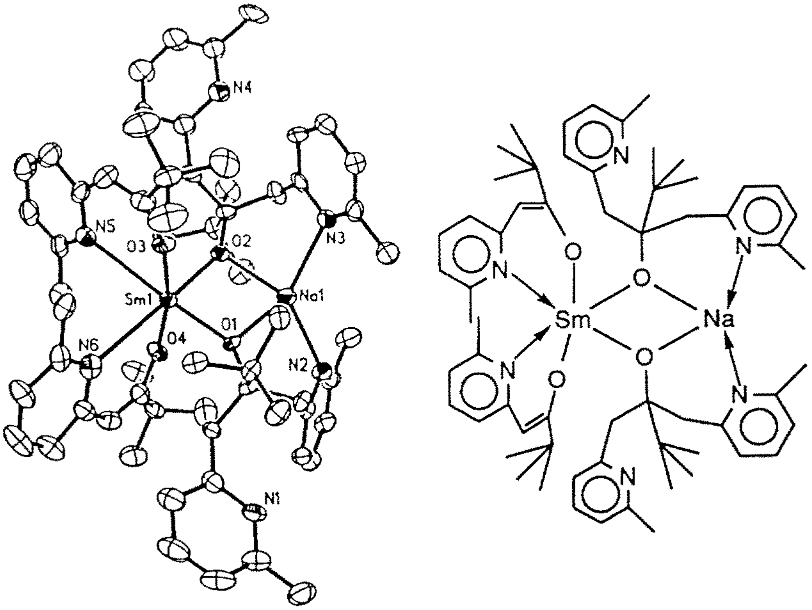
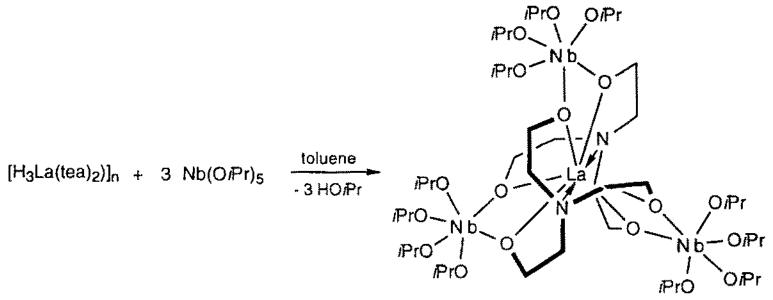


Fig. 21. Molecular structure of NaSm[OCtBu(2-CH$_2$-NC$_5$H$_3$-6-Me)$_2$]$_2$[OC(CMe$_3$)=(2-CH-NC$_5$H$_3$-Me-6)]$_2$ [127]

Another alkali metal inclusion was observed in the mixed alkoxide *ate* complex NaSm[OCtBu(2-CH$_2$-NC$_5$H$_3$-6-Me)$_2$]$_2$[OC(CMe$_3$)=(2-CH-NC$_5$H$_3$-Me-6)]$_2$ [127]. The complex was formed from the Sm(II) amide NaSm[N(SiMe$_3$)$_2$]$_3$ with slight excess of the doubleclinching alcohol. The elimination of 2,6-dimethylpyridine shows another option of this ligand system. Both mono- and doubleclinching ligands are now present and produce a distorted octahedral geometry at the samarium center in which the bidentate enolate ligands are oriented such that the pyridyl donors are *cis* to each other and the oxygen donors are *trans* (Fig. 21, Table 10).

CHdo-alcohols can assist in retaining homogeneity of heterobimetallic alkoxide complexes at a molecular level. Denucleation is often observed as in $La(tea)_2[Nb(O\textit{i}Pr)_4]_3$ which was synthesized by dissolving insoluble "$H_3La(tea)_2$" in the presence of $Nb(O\textit{i}Pr)_5$ in toluene (Eq. 11, Table 10) [136]. The product is even sublimable at 180–250 °C / 10^{-1} torr without decomposition. The $La(tea)_2$-core assembles the three $Nb(O\textit{i}Pr)_4$ moieties via the alcohol functionalities. Two deprotonated tea ligands form a nearly regular bicapped trigonal antiprism around lanthanum with the nitrogens capping both bases of the prism.



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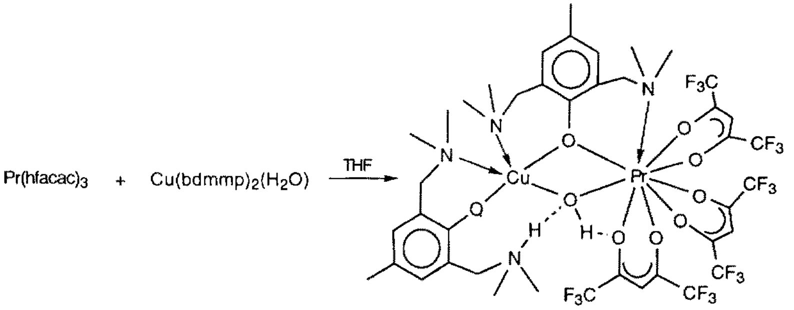
Deoligomerization of decameric $[Y(OCH_2CH_2OMe)_3]_{10}$ was achieved by treatment with the mixed alkoxide/β-diketonate copper complexes $[(L)Cu(OCH_2CH_2OMe)]_4$ (L = thd, hfacac; Scheme 13, Table 10) [137]. In the monoyttrium complex $[(thd)_4Cu_3Y(OCH_2CH_2OMe)_5]$ the metals are linked by the five 2-methoxyethoxide ligands. One thd ligand was transferred to the yttrium atom accomplishing 8-coordination. In situ prepared $[(hfacac)_2Y(OCH_2CH_2OMe)]_n$ yields a YCu_2-complex which also contains an 8-coordinated yttrium center. The varying Y : Cu ratios have been discussed in terms of the stereoelectronic influence of different co-ligands.

The bridging aryloxide ligand in $PrCu[OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4][HOC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4](\mu\text{-}OH)(hfacac)_3$ is donating to both copper and praseodymium with the amino functionalities (Eq. 12, Table 10) comparable to the Lu-Na complex shown in Eq. (10). The coordination sphere around praseodymium is completed by three original hfacac and one hydroxo ligand. The latter was most likely formed by deprotonation of water by dangling Lewis basic amino groups [138]. LnCu- and $LnCu_2$- complexes containing 1,3-bis(dimethylamino)-2-propoxide as bridging moiety were synthesized similarly [139]. The structural arrangement of $LaCu_2(bdmap)_3(O_2CCF_3)_4$ is depicted in Eq. (13). The lanthanum ion accomplishes an irregularly polyhedral 9-coordination. The presence of hfacac as co-ligand resulted in a remarkable hfacac degradation. Due to its relevance in organic synthesis this topic is discussed later (Sect. 6.2.3) [140].



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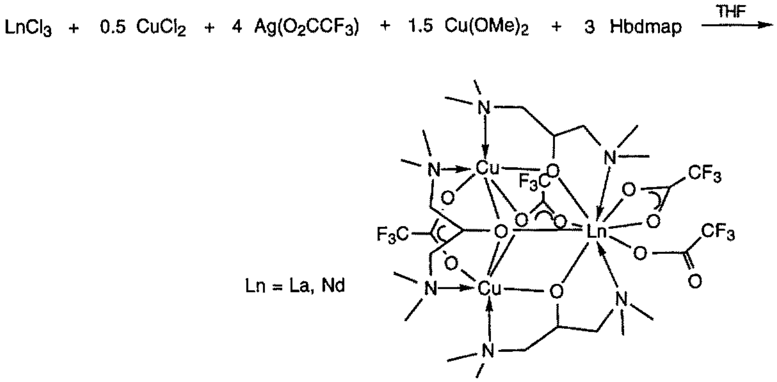
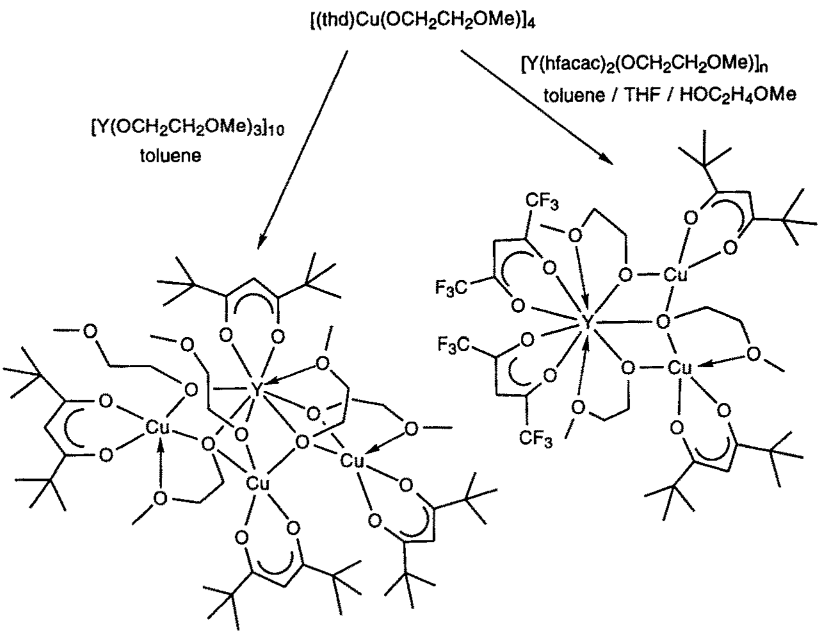


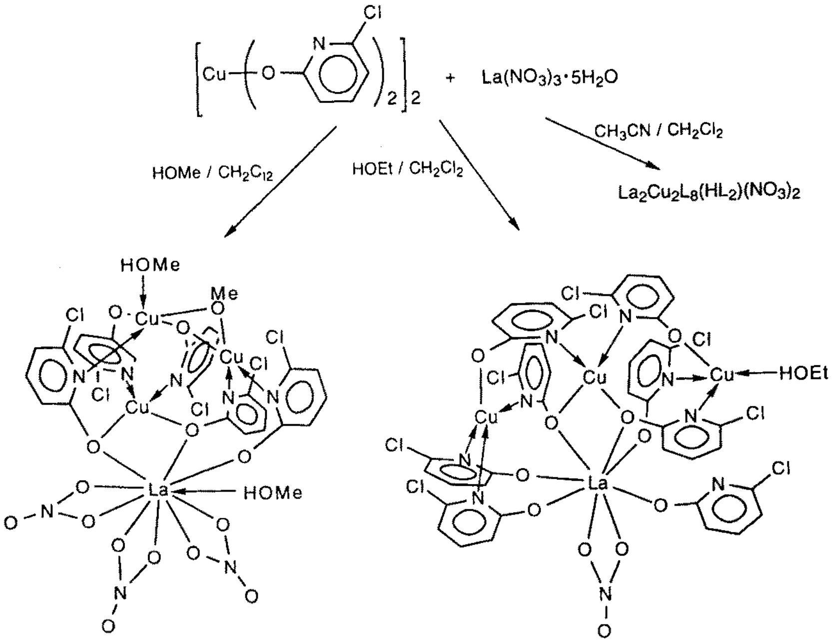
(13)

The assembling tendency of donorfunctionalized ligands was investigated in detail in heterobimetallic complexes derived from hydroxypyridine and the anion of 2-pyrrolidone. The diversity of structural types is controlled inter alia by solvent, kind of 6-substitution of the pyridine ring, type of additional counterions and work up procedures. Ln_xCu_y-complexes derived from hydroxypyridine exhibit Ln:Cu ratios of 1:3, 2:2, 2:4, 2:8, 4:4 and 8:12 [141–144]. The anion of 2-pyrrolidine forms polymeric macrocyclic chain structures of type $\{LnHg_2\}_n$ and $\{Ln_2Hg_3\}_n$ dependent on the size of the lanthanide element [145].

The monolanthanum complexes as shown in Scheme 14 clearly demonstrate the influence of the solvent on product composition [141]. Here, 10- and 8-coordinate lanthanum is found in the methanol and ethanol reaction, respectively. The hydroxypyridine ligand can act both trinucleating with the exocyclic oxygen bridging La and Cu and the ring nitrogen contacting another Cu, and binucleating with the oxygen bound to La and nitrogen bound to Cu.



Scheme 13. Synthesis of mixed ligand yttrium/copper complexes [137]



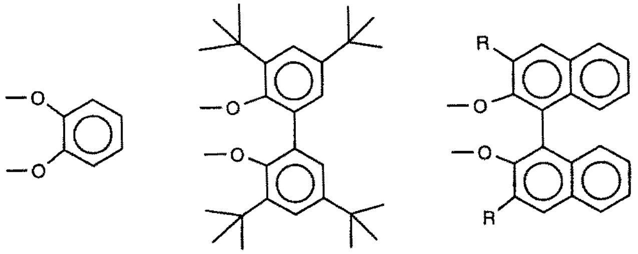
Scheme 14. Hydroxypyridine as an assembling ligand – solvent effects [141]

4.2 Divalent Ligands

The common methods of preparation of higher functionalized alkoxide complexes already reflect the increased kinetic stability of these systems compared to their monovalent pendants. Exclusion of moisture is no longer obligatory. Both di- and higher valency ligands as Schiff bases [89, 146] or calixarens [147] are suitable for synthesizing homo- or heterobimetallic complexes which are of interest in the design of magnetic materials and in heterogenous catalysis. Furthermore, they are used as mimics for the active site of metallo-enzymes and metallo-proteins. Due to their luminescent properties lanthanide ions are introduced as spectroscopically active substitutes for essential Ca^{2+}, which is similar in size and chemical properties [148, 149].

Formally, divalent ligands L^{2-} accomplish charge balanced, homoleptic, monomeric complexes of the oxidation states II and IV. Isolation of putative Ln(II)L species will require several Do groups. 1:2 Complexation in CeL_2 should be more easily accomplished. Stabilization of Ce(IV) is well established in such ligand environments as shown in $Ce(acac)_4$ [150]. With respect to Ln(III), complexes of type Ln_2L_3 or monomeric LnL(HL) and *ate* complexes $M(I)LnL_2$ could be expected. 8-Coordination in LnL(HL) and CeL_2 complexes (L with several Do groups) would usually involve a stereochemistry with the limiting polyhedrons square antiprism, dodecahedron or bicapped trigonal prism. A very promising option of the L^{2-} ligand system is its use as a rigid, stabilizing co-ligand in heteroleptic complexes analogous to the well known "Cp_2LnR" systems [151] by replacement of two Cp^- by one L^{2-} ligand.

Impressive coordination ability of divalent phenolic ligands (Fig. 22, Table 11) was demonstrated in homoleptic catecholato derivatives [152]. Surprisingly, Ce(IV) was not reduced by the catechol dianion. In addition, the low solubility of the complex $Na_4[Ce(C_6H_4O_2)_4] \cdot 21H_2O$ even permits its direct synthesis and crystallization from aqueous solutions (Eq. 14a, Table 11) [153]. The crystal structure consists of discrete 8-coordinate $[Ce(cat)_4)]^{4-}$ dodecahedra. Each sodium is coordinated to two nonequivalent oxygens from two catecholato



catecholato

biphenolato

binaphtolato
(R = H, $SiPh_3$)

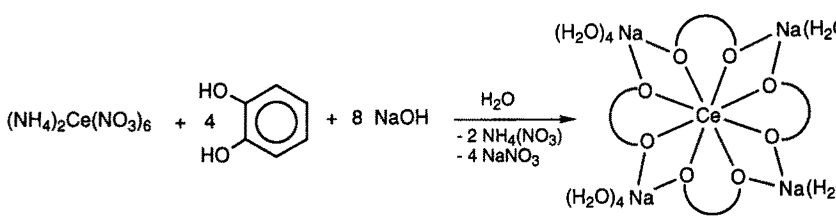
Fig. 22. Phenolic divalent ligands

Table 11. Lanthanide CHdo-alkoxides with divalnt ligands

Complex	Ln–O [Å]	β [°]	Ref.
$Na_4[Ce(C_6H_4O_2)_4] \cdot 21H_2O$	2.357(4), 2.362(4)	68.3(1)	[153]
$Na_5[Gd(cat)_4] \cdot 19.2H_2O$	2.393(2), 2.422(2)	68.05(6)	[154]
$La[1,1'\text{-}(2\text{-}OC_6H_2tBu_2\text{-}3,5)_2][CH(SiMe_3)_2](THF)_3$	2.216(7), 2.271(9)	88.1(3)	[157]
$Na_3Pr((S)\text{-}BINOL)_3 \cdot 6THF \cdot H_2O$	2.365, 2.386	—	[158]
$Na_3Nd((S)\text{-}BINOL)_3 \cdot 6THF \cdot H_2O$	2.338, 2.363	—	[158]
$Na_3Eu((S)\text{-}BINOL)_3 \cdot 6THF \cdot H_2O$	2.286, 2.312	—	[158]
$[YL_2][NH_4](H_2O)^a$	2.264(4)–2.322(5)	67.9(1)–68.7(2)	[159]

[a] L is shown in Eq. (14c), N-Y-N [°]: 65.1(1), 66.5(2)

ligands and to four water oxygens. All 21 waters contribute to a hydrogen bonded network through the crystal.



(14a)

Lanthanide(III) catecholates exhibit a complex coordination chemistry in aqueous solution [154]. While at neutral pH, 1:1 complexes are present in solution, higher pH values (pH > 11) favor 2:1, 3:1 and 4:1 catechol:metal stoichiometries as shown in $\{Na[Gd(cat)_2] \cdot 10H_2O\}_n$, $Na_6[Ln(cat)_3]_2 \cdot 20H_2O$ (Ln = Gd, Ho) and $Na_5[Gd(cat)_4] \cdot 19.2H_2O$. The latter monogadolinium complex is isomorphous with the cerium(IV) complex (Table 11). The change of the metal charge from Ln(IV) to Ln(III) now requires a fifth sodium cation which is disordered over several sites in the cell.

Though chiral biphenolate and binaphtholate complexes of the maingroup and d-transition metals are well established "synthetic utilities" in enantioselective synthesis [155, 156], the first corresponding lanthanide complexes were synthesized very recently. $La[1,1'\text{-}(2\text{-}OC_6H_2tBu_2\text{-}3,5)_2][CH(SiMe_3)_2]$ is formed by the mild protonolysis reaction of $La[CH(SiMe_3)_2]_3$ with the phenol component [157]. The molecular structure of the *tris*-THF adduct reveals a highly distorted octahedral geometry around the lanthanum metal with the three THF ligands in facial position (Fig. 23, Table 11).

The stereochemically more rigid BINOL ligand afforded the chiral complex $La[1,1'\text{-}(2\text{-}OC_{10}H_5SiPh_3\text{-}3)_2][CH(SiMe_3)_2](OEt_2)$ whose diastereotopic $SiMe_3$ groups were shown by NMR. Reaction with excess CO resulted in CO insertion into the La-C σ-bond and 1,2 $SiMe_3$ migration yielded the mixed enolate/naphtholate complex $La[OC(SiMe_3){=}CHSiMe_3][1,1'\text{-}(2\text{-}OC_{10}H_5SiPh_3\text{-}3)_2]$.

As in the case of the catecholate ligands the complexation of dianionic BINOL ligands can be achieved under aqueous conditions (Eq. 14b, Table 11).

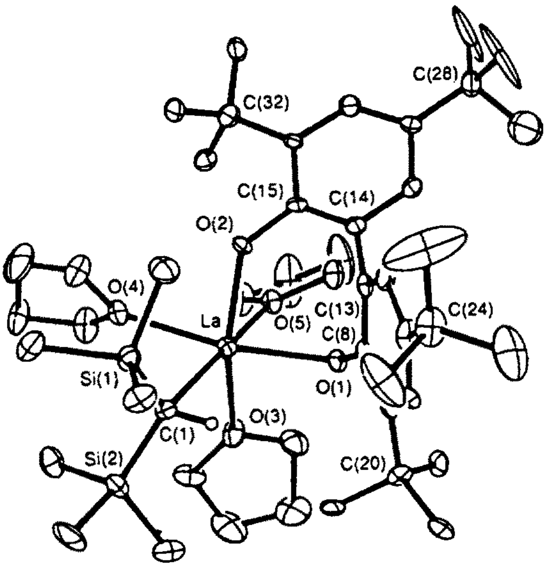
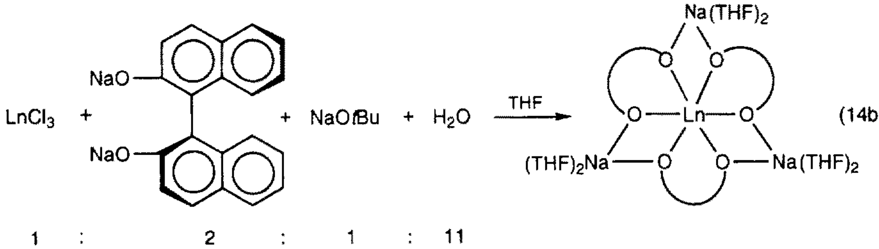


Fig. 23. Molecular structure of La[1,1′-(2-$OC_6H_2tBu_2$-3,5)$_2$] [$CH(SiMe_3)_2$]$(THF)_3$ [157]

Asymmetric *ate* complexes of type $Na_3Ln((S)\text{-BINOL})_3 \cdot 6THF \cdot H_2O$ (Ln = Pr, Nd, Eu) could be crystallized from THF and exist only in the Λ-form [158]. Their stability against moisture had an enormous impact on application of lanthanide alkoxides in organic synthesis (Sect. 6.2.1).



(14b)

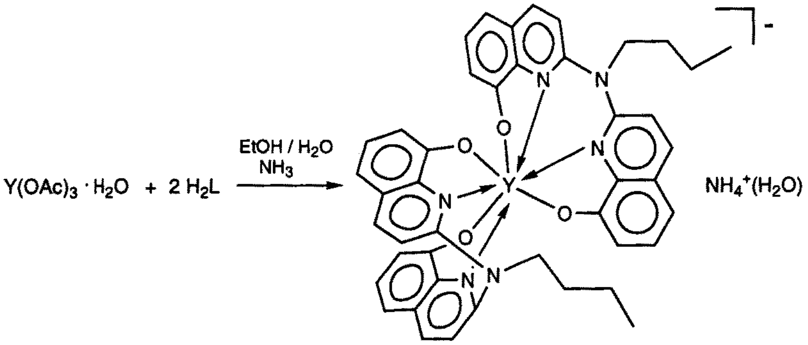
Table 12. Mononuclear Schiff base complexes

Complex	Ln–O [Å]	β [°]	Ref.
[Er(salen)$_2$][pipH]	2.22(1), 2.23(1), 2.28(1), 2.35(1)	69.4(5), 71.6(4), 72.5(4), 74.2(5) 65.4(5)[a], 67.0(5)[a]	[166]
Eu(salen)(Hsalen)	2.24(2), 2.28(2), 2.33(2), 3.35(2)	67.2(7), 68.1(6), 69.3(7), 74.7(8) 66.8(8)[a], 67.5(7)[a]	[167]
Ce(dsp)$_2$	2.187(4), 2.213(3), 2.224(3), 2.235(3)	69.4(1), 69.7(1), 69.9(1), 70.2(1) 60.5(1)[a], 61.3(1)[a]	[168]
Ce(fluoridene)$_2$	2.196(2), 2.200(2), 2.219(2), 2.230(2)	70.06(9), 70.19(8), 70.21(9), 70.82(9), 66.0(1)[a], 66.39(9)[a]	[169]
LuL(H_2O)[b]	2.159(9), 2.219(9)	—	[170]

[a] N-Ln-N

[b] L is shown in Eq. (15)

Quinolato moieties which are linked by a butylamino group afford a powerful tetradentate ligation mode as realized in an 8-coordinate, anionic yttrium complex (Eq. 14c) [159]. Two ammonium ions and two water molecules link two complex anions to form associates of type $[(NH_4)YL_2 \cdot H_2O]_2$ in the solid state.



(14c)

4.2.1 Schiff Base Ligands

Schiff bases offer a versatile and flexible ligand environment for the lanthanide elements, including stability in aqueous or non-aqueous solvents, variety of functionality sites, stabilization of particular coordination geometries or particular oxidation states, etc. [160].

Depending on the experimental conditions, Schiff bases (alcohols, phenols) often act as neutral ligands occupying the next coordination environment of the lanthanide cations, while the counterions are separated from the metals in the secondary coordination sphere [89]. The scope and topic of this review will focus on complexes with anionic Schiff base ligands [161–165]. Synthesis strategies of various species derived from the very classic salen-type ligands (Fig. 24, Table 12) include base (MOH, NR_3)-promoted ligand exchange and template condensation reactions (Scheme 15).

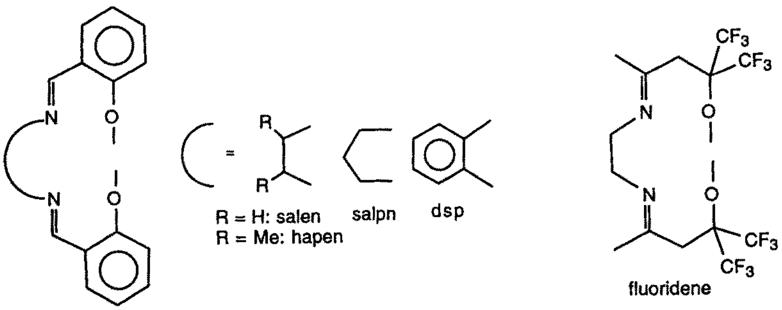
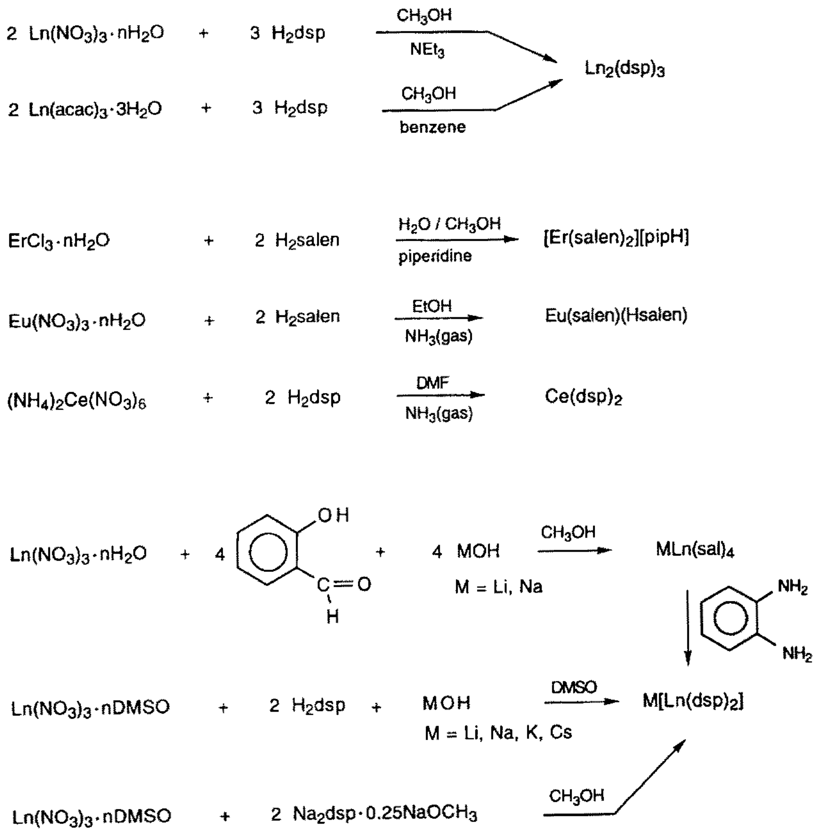


Fig. 24. Divalent Schiff base CHdo-alcohols (salen = *N*,*N*′-ethylene-bis(salicylideneimine); hapen = *N*,*N*′-ethylene-bis(*o*-hydroxyacetophenoniminato); salpn (saltn) = *N*,*N*′-propylene-bis(salicylideneimine); dsp = disalicylidene-1,2-phenylene-diamine; fluoridene = 1,1,1,12,12,12-hexafluoro-2,11-bis(trifluoromethyl)-4,9-dimethyl-2,11-diolato-5,8-diazadodeca-4,8-diene

Mononuclear Er(salen)$_2$(pipH) consists of [Er(salen)$_2$]$^-$ anions and pipH$^+$ cations [166]. Every eight donor atoms of two tetradentate salen ligands are involved in the formation of a distorted square antiprismatic geometry at the metal atom. The piperidinium ion forms strong hydrogen bonds with two oxygen atoms (N-O 2.75, 2.83 Å). Eu(salen)(salenH) exhibits a similar dodecahedral geometry [167]. A short N-O distance of 2.64 Å indicates the existence of a hydrogen bond.

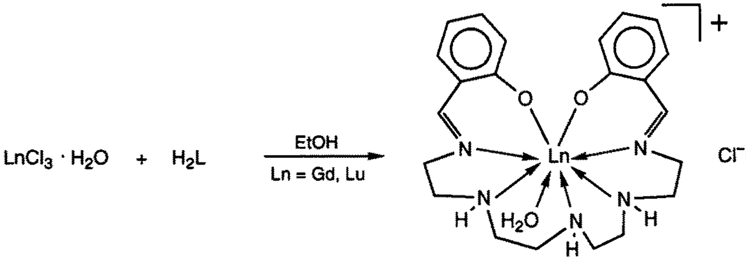
A square antiprismatic arrangement determines the stereochemistry in neutral Ce(IV) complexes like Ce(dsp)$_2$ [168] and Ce(fluorodine)$_2$ [169]. The latter complex was prepared by a remarkable template reaction involving the oxidation of Ce^{3+} to Ce^{4+} (Scheme 16).

Monocationic Schiff base complexes of gadolinium and lutetium were obtained by employing a highly aminofunctionalized Schiff base ligand as shown in Eq. (15) [170]. An X-ray structure analysis of the lutetium complex revealed discrete cations and a distorted square antiprismatic coordination polyhedron.



Scheme 15. Synthesis of salen-type complexes

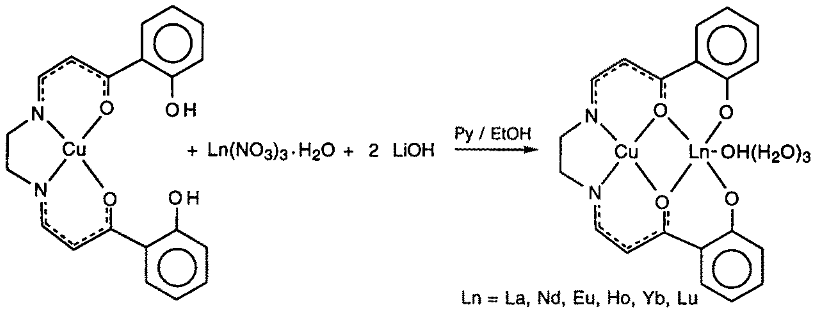
The gadolinium derivative was discussed as a potential agent in Magnetic Resonace Imaging [R_1(20 MHz, 37°C) = 3.91 mmols^{-1}].



(15)

A broad application of phenolic Schiff base ligands lies in the synthesis of heterobimetallic complexes. Extended functionalization of the L^{2-} ligand affords the so-called "compartmental" ligands which ensure rich coordination chemistry by accomodation of several metals [89, 146]. Some representative ligands are depicted in Fig. 25.

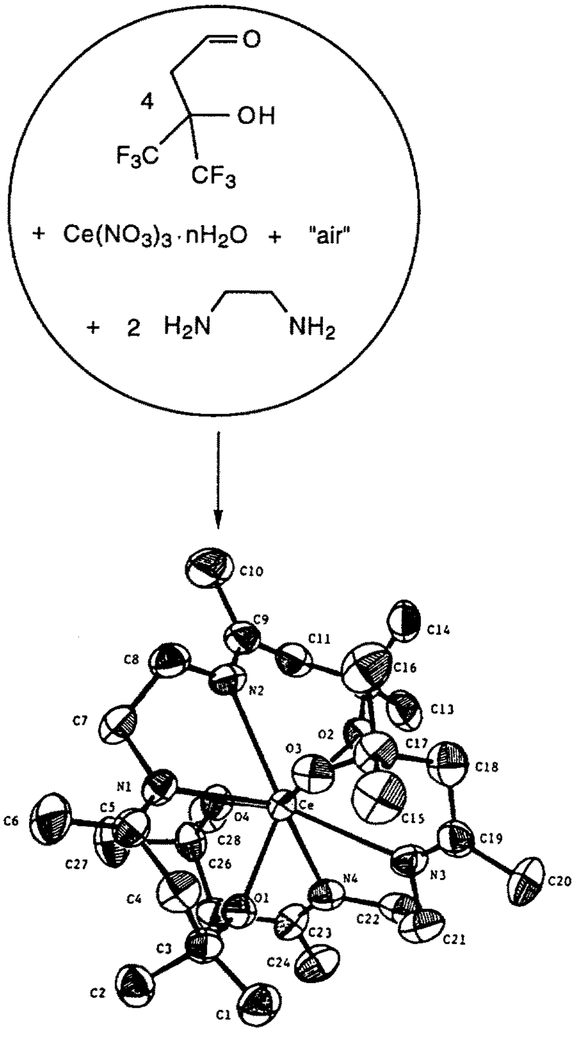
Heterobimetallic CHdo-alkoxides have already been discussed in Sect. 4.1.3. However, Schiff base derived systems originally dominated this topic [89]. Homo- and heterodinuclear complexes as well as tris-, tetra- and hexanuclear clusters of type [$LnM(II)_2$], [$Ln_2M(II)_2$] and [$Ln_2M(II)_4$], respectively, were reported. Usually a M(II) Schiff base complex is directly employed as ligand as exemplified in Eq. (16) [171, 172]. Alkoxide bridge formation is commonly observed. Complexes exhibiting the "Gd_xCu_y" metal constellation allowed the detection of ferromagnetic coupling on a molecular level [173–175]. In the course of these detailed investigations, one- and two-dimensional lanthanide-copper systems were also obtained [176].



(16)

Structurally characterized monolanthanide species include $Ce(NO_3)_3[Cu(salpn)]_2$(Ce-O: 2.40(1)–2.55(1) Å) [177], {$Gd(H_2O)_3[Cu(hapen)_2]$}$(ClO_4)_3$ (Gd-O: 2.35(4), 2.39(1) Å) [178], {$Gd(H_2O)_3[Cu(salen)_2]$}$(ClO_4)_3$ (Gd-O: 2.30(2)–2.44(2) Å) [178] and $Gd(H_2O)(NO_3)_3[Cu(salpn)]_2$ (Gd-O: 2.38(3)–2.53(5) Å) [179].

The usually observed low solubility of Schiff base complexes hampers their industrial use in separation techniques. Introduction of bulky organic substituents into the phenyl rings [162] or attachment of aliphatic chains at nitrogen positions [180] are procedures to enhance considerably their solubility (Fig. 26).



Ce(fluorodine)$_2$

Scheme 16. One pot synthesis and molecular structure of Ce(fluoridene)$_2$ [169]

4.3 Higher Valency Ligands

4.3.1 Trivalent Ligands

This type of ligand can afford charge balanced, 1:1 complexes with lanthanide elements in their most stable oxidation state III (Table 13). Alkoxide complexes of the triethanolamine ligand were reported as insoluble, high melting (> 360 °C) oligomerized materials [91–93]. Substituted "atrane" complexes did

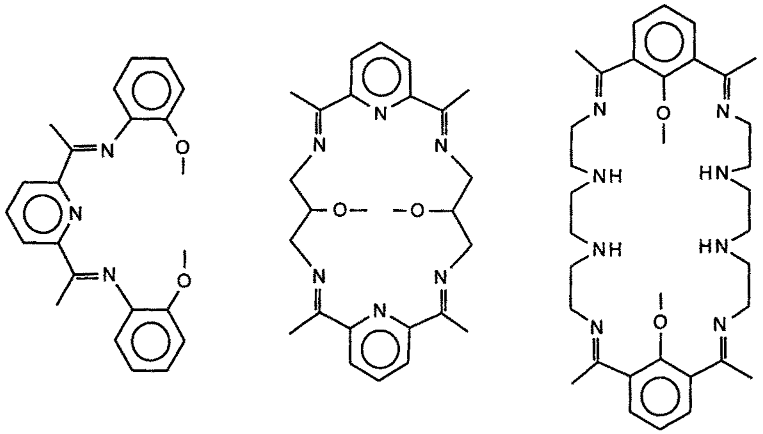


Fig. 25. Extended functionalization in divalent Schiff base ligands

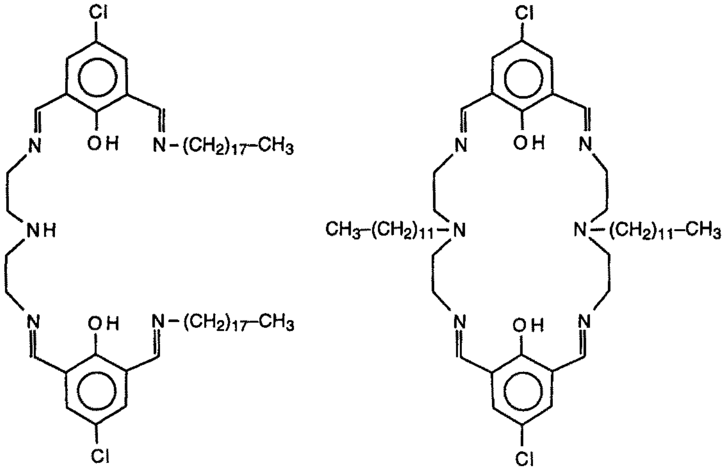


Fig. 26. Tailoring of Schiff base ligands with aliphatic groups

Table 13. Lanthanide complexes derived from higher valency ligands

Complex[a]	Ln-O [Å]	β [°]	Ref.
Yb(trac)	2.161(9) – 2.199(9)	75.2 (4), 75.9(4), 77.2(4) 68.2(4)[b], 69.0(4)[b], 69.8(4)[b]	[184]
Yb(1,2,4-btt)	2.145(3), 2.160(3) 2.170(3)	77.8(1), 80.0(1), 80.4(1) 68.2(1)[b], 69.6(1)[b], 70.2(1)[b]	[186]
$Gd(H_3trac)(NO_3)_3$	2.337(2), 2.342(2) 2.344(2)		[183]
$[Eu(H_6L)(NO_3)(DMF)_4]\cdot 3DMF$	2.26(1), 2.32(1)	91.1(4)	[192]
$Eu(H_4L')(OH)(DMF)_6$	2.35(1)	–	[193]
$[Gd(H_3L'')(NO_3)]NO_3\cdot 3H_2O$	2.14(1)	–	[196]

[a] Ligands L, L′, L″ are referenced to in the text
[b] N-Ln-N

not appear in the literature [181]. However, Schiff base ligands like H_3trac, H_3hatren and H_3datren yielded mononuclear 7-coordinate LnL-type complexes (Fig. 27, Table 13) [182]. Kind of solvent and Ln-precursor, respectively, determine the type of ligand coordination. Type II coordination was obtained by the reaction of $Ln(NO_3)_3(H_2O)_x$ or $LnCl_3(H_2O)_x$ with the ligand [183].

Solvent free "LnL" complexes (Type I) resulted from the silylamide route [184]. Crystals of Yb(trac) could be grown by sublimation (180 °C/10^{-2} Torr). The heptadentate ligand is wrapped around the ytterbium emerging in a disordered geometry. Both enantiomers, the right- (Δ) and left-handed (Λ) screw, are present in the unit cell.

KBH_4 reduction of phenolsubstituted H_3hatren-type Schiff base ligands produces potentially hexavalent aminophenol ligands. Reaction of excess of these ligands can also afford LnL complexes which are quite air stable. However, X-ray study of the gadolinium complex revealed a homodinuclear alkoxide complex with single O-atom bridges [185]. Five-membered imidazoline rings formed in Schiff base condensation reactions are opened during borohydride reduction (Scheme 17) [186].

The different products which are obtained due to hydroxybenzyl migration can be trapped by metal complexation. The thus formed trivalent, N_4O_3-encapsulating ligand adopts a pentagonal bipyramidal geometry at the ytterbium center with two aryloxide oxygens in the axial positions.

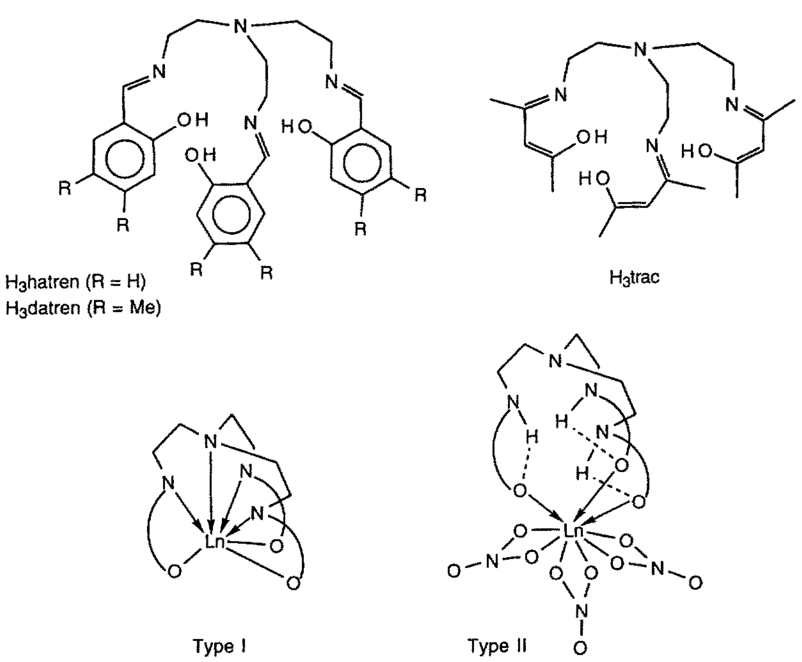
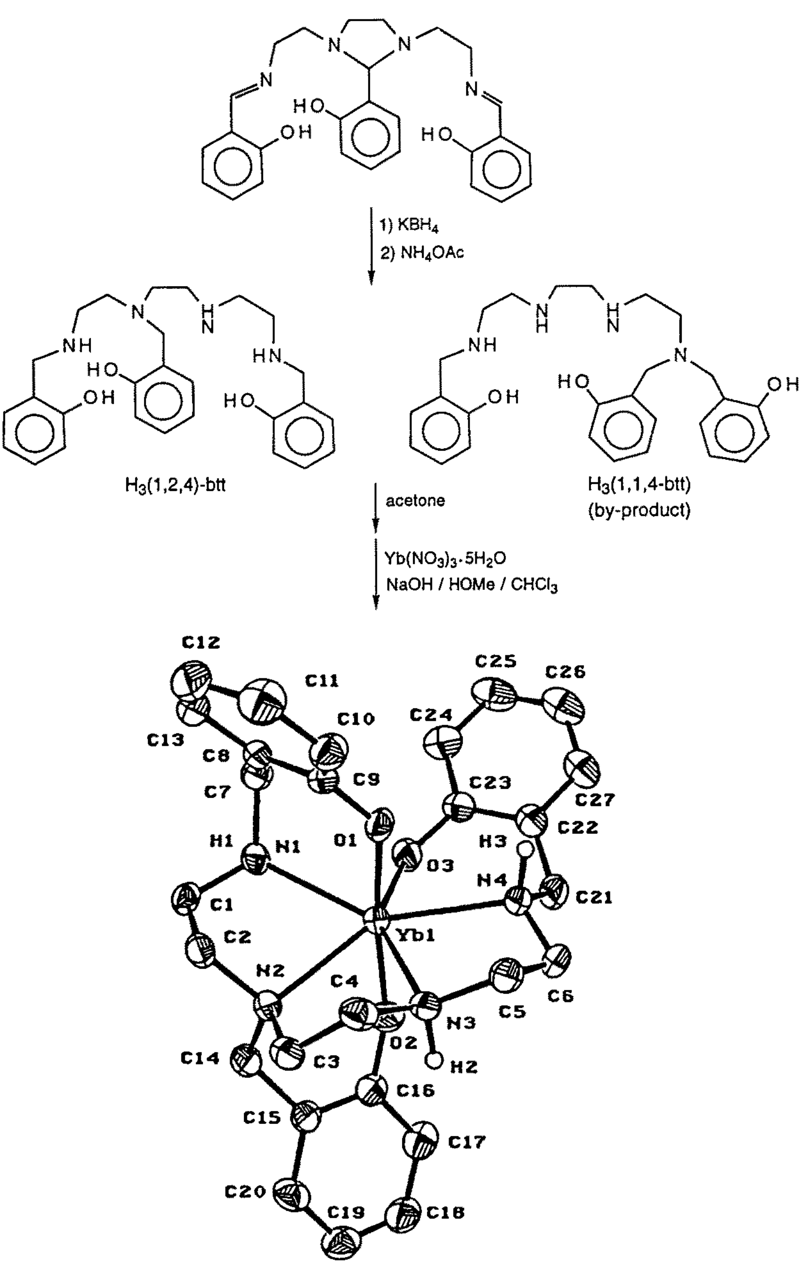


Fig. 27. Trivalent CHdo-alcohols and their mononuclear complexes



Scheme 17. Synthesis and molecular structure of Yb(1,2,4-btt) [186]

Figure 28 shows another two examples of trivalent Schiff base ligands. The macrocyclic ligand was generated in a template condensation of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in the presence of lanthanide salts [187]. The $La(NO_3)_3 \cdot H_2O$-reaction yielded a trinuclear complex of composition $[La_3L(\mu_3\text{-}OH)(OH)(NO_3)_4] \cdot 7H_2O$ [188].

Complexes of the acyclic Schiff base ligand are assumed to oligomerize due to coordinative unsaturation [189]. A dinuclear composition was proven for Ln(III) complexes of trivalent oligosilsesquisiloxane ligands of type $T_7(OH)_3$ (Fig. 28). Surprisingly, Si-O-Si frame sites can support additional coordination sites [190].

4.3.2 Higher Valency Ligands

Well-examined complexes include derivatives of macrocyclic polyphenols known as calixarenes [147] (Fig. 29, Table 13). Lanthanide complexes containing up to eight phenolic units (calix[8]arene) were reported.

Homo- and heterobimetallic complexes of the lanthanides are routinely observed with the large calix[8]arene [191]. However, this extended highly functionalized cavity can also accommodate just one lanthanide ion as shown in $[Eu(H_6L)(NO_3)(DMF)_4] \cdot 3DMF$ (H_8L = *p-tert*-butylcalix[8]arene, Table 13) [192]. Only two adjacent phenolic OH groups were deprotonated according to

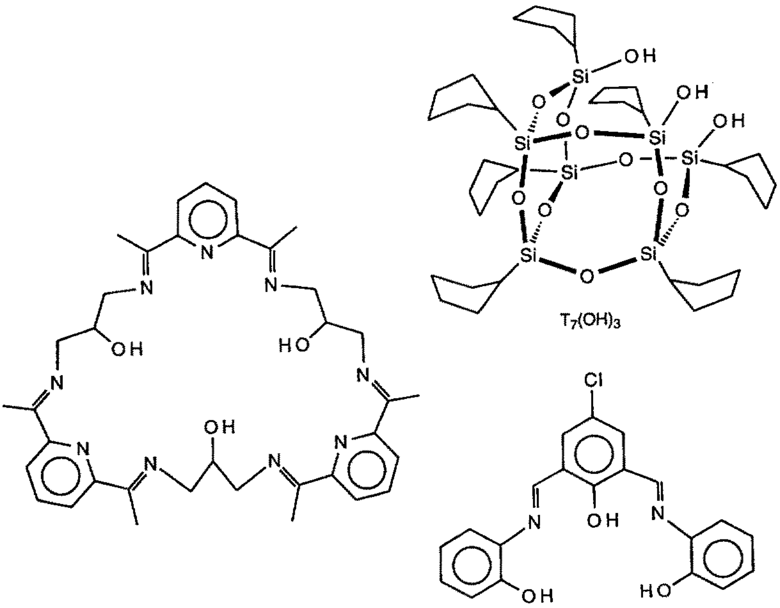
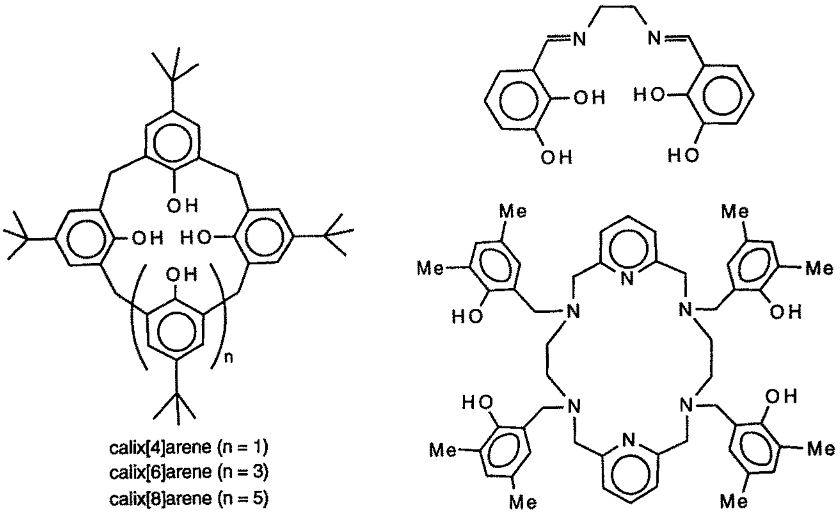


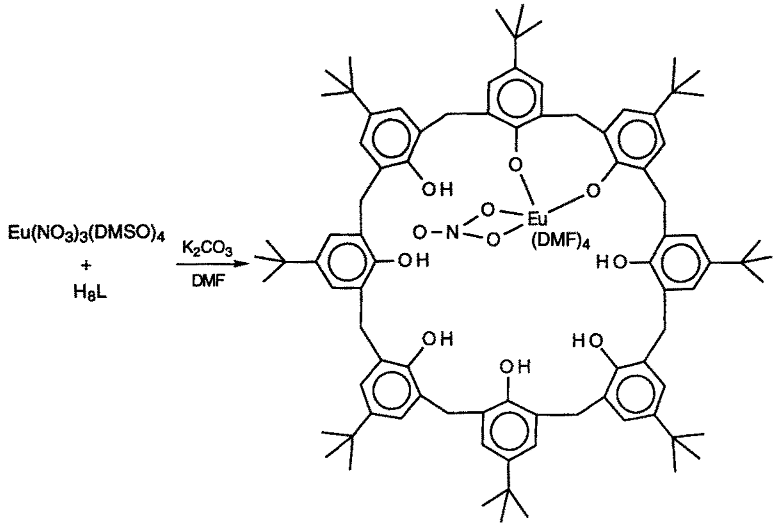
Fig. 28. Trivalent Schiff base and siloxide ligands



calix[4]arene (n = 1)
calix[6]arene (n = 3)
calix[8]arene (n = 5)

Fig. 29. Polyvalent systems

Eq. (17) and act in a bidentate fashion. The third charge is balanced by a bidentate nitrate ligand and four DMF ligands complete the 8-coordination.



(17)

The structural characterization of a mononuclear Eu-calix[6]arene complex reveals a more unusual complexation mode. In $Eu(H_4L)(OH)(DMF)_6$ (H_6L = *p-tert*-butylcalix[6]arene; Table 13) the Eu cation is placed outside the cavity forming only one monodentate bond to the calixarene ligand [193]. Six DMF molecules and most likely a hydroxyl group accomplish 8-coordination. The smaller sized calix[4]arene [194] and ether-extended bis(homooxa)-*p-tert*-

butylalix[4]arene [195] yield dinuclear complexes of type $[Eu_2(HL)_2]$ (e.g. H_4L = *p-tert*-butylcalix[4]arene) where the metal centers are bridged by two phenolate moieties.

Hexaazamacrocycles substituted with four phenolic groups (Fig. 29) provide another multi(tetra)valent environment in the gadolinium complex $[Gd(H_3L)(NO_3)]NO_3 \cdot 3H_2O$ (Table 13) [196]. In the solid state the nitrogen macrocycle adopts a chair conformation around the gadolinium with all nitrogens coordinating. One phenolic oxygen which forms the shortest lanthanide-ligand contact and a bidentate nitrate ligand accomplish 9-coordination. Macrocyclic gadolinum complexes are promising contrast agents in magnetic resonance imaging (MRI) and the present complex shows a remarkable relaxivity ($8.2 \cdot 10^{-3}$ $dm^3mol^{-1}s^{-1}$/28 °C, 10 MHz).

5 Mixed Ligands – Cyclopentadienyl-Alkoxide Complexes

Due to the important role of the cyclopentadienyl ligand in organolanthanide chemistry, a separate section is dedicated to this topic. Mononuclear alkoxide complexes involving co-ligands such as Cl, NR_2, NO_3, etc. were treated in previous sections. Although the first unbridged alkoxide complexes of the larger lanthanide elements were obtained in the form of heteroleptic systems with the standard ligand cyclopentadienyl as co-ligand [197], the presence of the cyclopentadienyl ligand is not a guarantee for mononuclear species. The preferred formation of doubly bridged dinuclear complexes of type $Cp_2Ln(\mu\text{-}OR)_2LnCp_2$ is reflected in numerous structural determinations when OR is a small alkoxide [198] or enolate ligand [199]. By use of more bulky alkoxide, aryloxide or siloxide ligands monomeric complexes of type "$Cp_2Ln(OR)$" and "$CpLn(OR)_2$" could be accomplished (Table 14).

Table 14. Heteroleptic cyclopentadienyl-based complexes

Complex	Ln–O [Å]	Ref.
$(CpCH_2CH_2NMe_2)_2Nd(silox)$	2.179(2)	[207]
$Cp^*_2Nd[O(CH_2)_4C_5Me_5](THF)$	2.114(3)	[203]
$Cp^*_2Sm[O(CH_2)_4C_5Me_5](THF)$	2.08(1)	[202]
$Cp^*_2Lu[O(CH_2)_4C_5Me_5](THF)$	2.012(3)	[203]
$Cp^*_2Sm(OC_6HMe_4\text{-}2,3,5,6)$	2.13(1)	[197]
$Cp_2Nd(OC_6H_3Ph_2\text{-}2,6)(THF)_2$	2.239(8)	[206]
$Cp_2Yb(OC_{10}H_7)(THF)$	2.06(1)	[201]
$Cp^*Ce(OC_6H_3tBu_2\text{-}2,6)_2$	2.247(2), 2.258(2)	[209]
$Cp^*Y(OC_6H_3tBu_2\text{-}2,6)_2$	2.096(4), 2.059(3)	[210]
$Cp_3Ce(OtBu)$	2.045(6)	[212]

5.1 Dicyclopentadienyl Complexes

The 7-coordinate aryloxide complex $Cp^*_2Sm(OC_6HMe_4\text{-}2,3,5,6)$ was the first reported mononuclear dicyclopentadienyl lanthanide alkoxide obtained by reaction of $Cp^*_2Sm(THF)_2$ with the phenol (Table 14) [197]. Formally 9-coordinate $Cp_2Nd(OC_6H_3Ph_2\text{-}2,6)(THF)_2$ is formed from $NdCp_3$ with an equimolar amount of 2,6-diphenylphenol (Table 14). The two THF ligands occupy the axial positions of a markedly distorted trigonal bipyramid [200]. The 8-coordinate naphthoxide $Cp_2Yb(OC_{10}H_7)(THF)$ was synthesized analogously. A thermolysis study revealed dimerization with loss of THF and subsequent disproportionation (Scheme 18, Table 14) [201].

Attempted synthesis of $LnCp^*_3$ according to Scheme 19 resulted in THF cleavage and generation of a *n*-butoxide ligand terminally functionalized with pentamethylcyclopentadiene (Table 14) [202, 203]. The in situ generated alkoxide ligand is bonded in a monodentate fashion to the lanthanide elements.

Crystallization of $Cp_2LuPPh_2(THF)_2$ in THF also resulted in THF cleavage and formation of a biphenylphosphino functionalized *n*-butoxide which acts as a monodentate bridging alkoxide in $[Cp_2Lu(\mu\text{-}O(CH_2)_4PPh_2)]_2$ [204]. Although bonded in a chelating fashion the alkoxide ligands in $[Cp_2Yb(\mu\text{-}OCHMeCOO\textit{i}Bu)]_2$ and $[MeCp_2Yb(\mu\text{-}OCH_2(CH_2)_3O)]_2$ [205] cannot suppress the formation of an alkoxide bridged dinuclear complex. For comparison the carboxylate ligand in $Cp_2Y(\mu\text{-}O_2C(CH_2)_3NMe_2)$, which is also η^2-bonded, afforded a mononuclear complex [206].

Use of a flexible aminosubstituted cyclopentadienyl ligand afforded a mononuclear species with the bulky silox ligand as alkoxide component. Only one "donor arm" is required to achieve a sterically saturated 8-coordinated neodymium center (Fig. 30, Table 14) [207].

The formation of Ln-OR bonds in reactions involving cyclopentadienyl complexes and carbonyl compounds are discussed in Sect. 6.2.3 (Table 18).

Unusual coordination around potassium was observed in the 2-dimensional layered structure of the *ate* complex $\{K[Cp_2Nd(\mu\text{-}OC_6H_3Me_2\text{-}2,6)_2]\}_n$ [208]. No close K ··· O contact was found, however, aryloxide ligands bridge the metal centers through arene interactions as in homoleptic *ate* complexes [69].

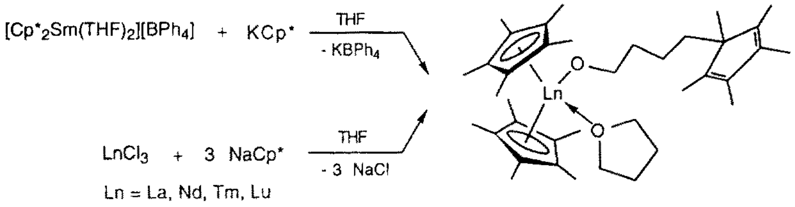
5.2 Monocyclopentadienyl Complexes

Mononuclear monopentamethylcyclopentadienyl complexes of cerium and yttrium were obtained according to Eq. (18) and are isostructural (Table 14)

$$6\,Cp_2Yb(OC_{10}H_7)(THF) \xrightarrow[-THF]{120\,C} 3\,[Cp_2Yb(OC_{10}H_7)]_2$$

$$\xrightarrow{230\,C} 4\,Cp_3Yb + 2\,Yb(OC_{10}H_7)_3$$

Scheme 18. Thermal degradation of $Cp_2Yb(OC_{10}H_7)(THF)$ [201]



Scheme 19. THF cleavage during attempted synthesis of $LnCp^*_3$

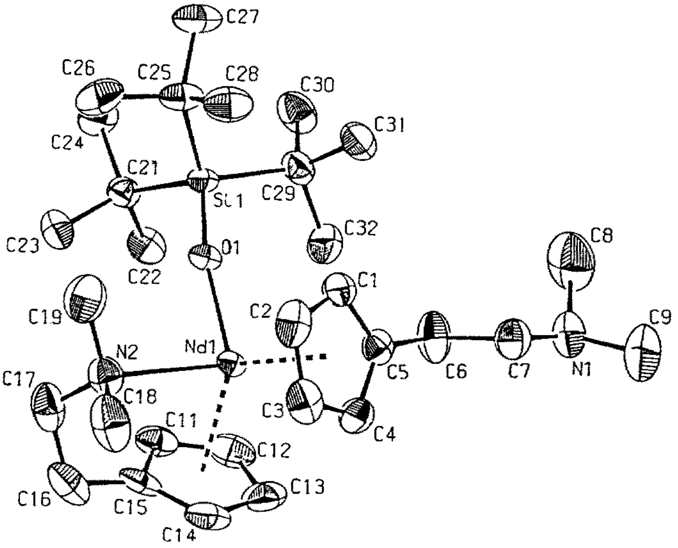


Fig. 30. Molecular structure of $(CpCH_2CH_2NMe_2)_2Nd(silox)$ [207]

[209, 210]. One of the aryloxide ligands exhibits an extremely small Ce-O-C angle of 105.0(2)° caused by a close Ce ··· C(*t*Bu) contact of 3.097(5) Å. Alkylation of $TCp^*Y(O_6H_3tBu_2\text{-}2,6)_2$ (Fig. 31) with $MCH(SiMe_3)_2$ (M = Li, K) and subsequent hydrogenation (20 bar, 25 °C) afforded the μ-hydride dimer $[Cp^*Y(OR)(\mu\text{-}H)]_2$ which can act as a single-component catalyst for the polymerzation of α-olefines and nonconjugated dienes (Sect. 6.1).

$$Ln(OAr)_3 + MCp^* \xrightarrow[80\text{–}100\,^\circ C]{\text{toluene}} Cp^*Ln(OAr)_2 + M(OAr) \qquad (18)$$

$$Ln = Ce\ (M = Li)$$

$$Ln = Y\ (M = K)$$

5.3 Ce(IV) Complexes

Alkoxide ligands provide a stabilizing coligation in Ce(IV) cyclopentadienyl complexes of type $Cp_3Ce(OiPr)$ [211], $Cp_2Ce(OtBu)_2$ and $Cp_3Ce(OtBu)$ [212].

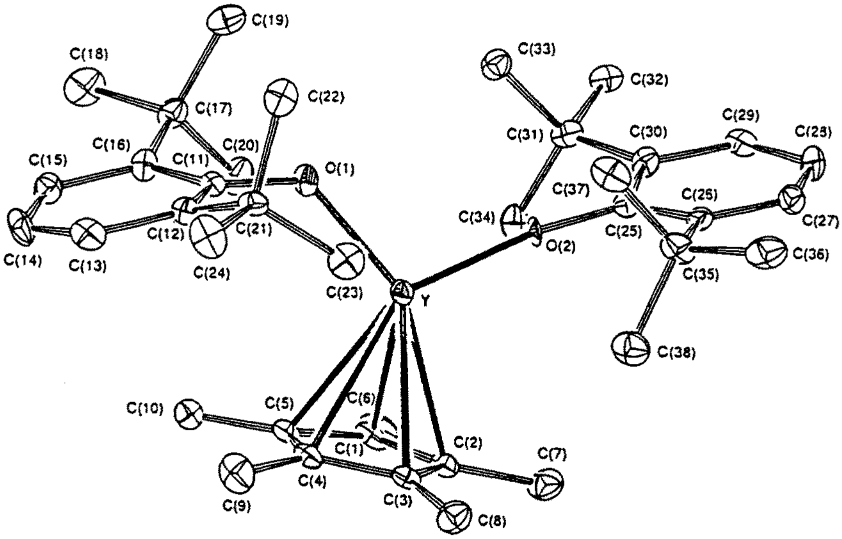


Fig. 31. Molecular structure of $Cp^*Y(OC_6H_3tBu_2\text{-}2,6)_2$ [210]

$Ce(OiPr)_4$ and mixed alkoxide/nitrate complexes were employed as precursors (Eqs. 19–21).

$$Ce(OiPr)_4 + 3\ Me_3SnCp \longrightarrow Cp_3Ce(OiPr) + 3\ Me_3Sn(OiPr) \qquad (19)$$

$$Ce(OtBu)_2(NO_3)_2(THF)_2 + 2\ NaCp \longrightarrow Cp_2Ce(OtBu)_2 + 2\ NaNO_3 \qquad (20)$$

$$2\ Ce(OtBu)(NO_3)_3(THF)_2 + 6\ NaCp \longrightarrow Cp_2Ce(OtBu)_2 + Cp_3Ce(OtBu) + 6\,NaNO_3 + \text{other products} \qquad (21)$$

Monomeric $Cp_3Ce(OtBu)$ could be separated from the reaction mixture by crystallization (Fig. 32, Table 14). The four ligands define a tetrahedron around the cerium atom with an almost linear Ce-O-C angle (176.3(6)°).

6 Applications

As a prelude to this section, intrinsic properties of the "Ln-OR" moiety will be passed in review. Alkoxide ligands are put into the category of hard ligands according the Pearson terminology and therefore optimally match the electropositive requirements of the "hard" lanthanide cations. The natural abundance of the lanthanide elements is the force behind the hard-soft relationship. The strongly electropositive and oxophilic character is expressed in high forma-

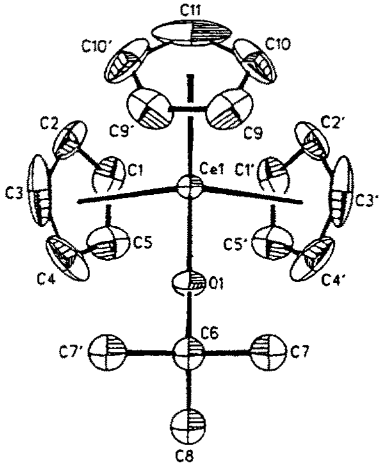


Fig. 32. Molecular structure of $Cp_3Ce(OtBu)$ [212]

tion enthalpies of the oxides (Ln_2O_3 $-1850\,kJmol^{-1}$) and the dissociation energies of gaseous monoxides, respectively [213]. This attraction contributes to the high thermodynamic stability of the Ln-OR bond whose short end lengths range is at approximately 2.00 Å for the smaller elements. Absolute bond disruption enthalpies D of organosamarium alkoxides have been determined in calorimetric titrations (O*t*Bu: D = 82.4 $kcalmol^{-1}$; $OCHtBu_2$: D = 81.3) [214].

At the very beginning of lanthanide alkoxide chemistry the insoluble derivatives of methanol and ethanol were described as predominantly ionic compounds [14b]. The high polarity of the lanthanide oxygen bond is caused by the large electronegativity difference between the oxygen (3.5) and the lanthanide elements (1.0–1.2) [215]. The charge localization causes kinetic lability and nucleophilic attack at the metal and electrophilic attack at the oxygen is favored. On the basis of these electronegativity differences the method of Hannay and Smyth came to 59% of ionic character [216] . However, this procedure does not consider the alkyl groups of the alkoxide ligand. Extended alkyl substitution of the alkoxide ligand as in tritox should reduce the ionic bond character by + I-effect. Although exhibiting typically covalent characteristics such as volatility and solubility in aliphatic and aromatic solvents, alkoxide complexes fit in the evaluation criteria for ionic compounds proposed by Raymond and Eigenbroth [217]. According to this structure formalism "··· bond lengths for a series of structurally similar compounds will follow systematically from their *ion size* and coordination number – that is ionic radii can be used to predict bond lengths". Therefore, this bond length criterion implies, that the difference between the metal-to-oxygen distance and the ionic radius of the metal, which is the effective alkoxide radius R_{ef}(alkoxide), should be constant. Figure 33 represents the structural data which have been available for the different classes of lanthanide alkoxides, considering monomeric and dimeric complexes which

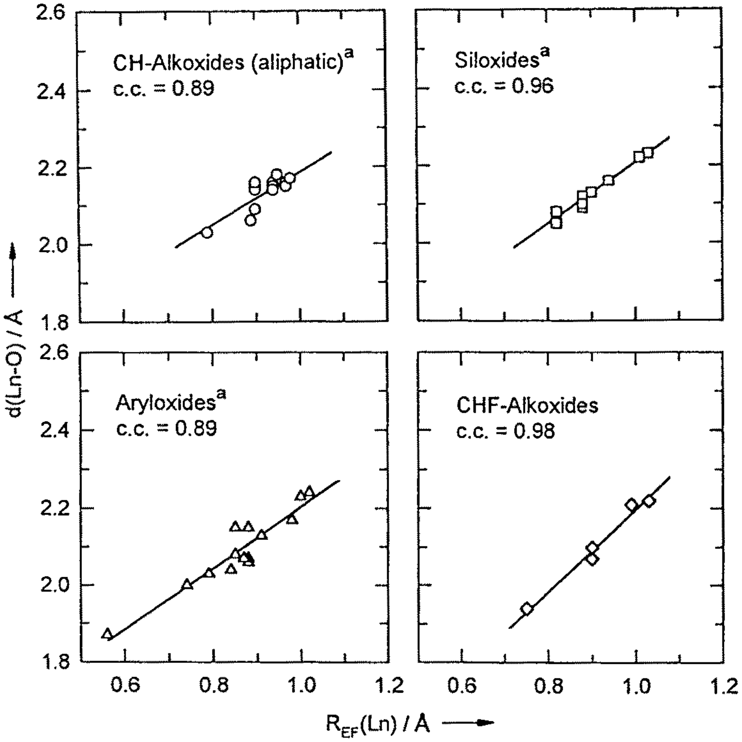


Fig. 33. Plots of the average terminal Ln-O(OR) distance for the different series of alkoxide structures;
[a] donor-functionalized species are included

contain only alkoxide ligands as counter-ligands [39]. The results of a regression analysis, as a mean to evaluate the deviation of ionic character, reveal relatively high correlation coefficients (c.c.) for siloxide and CHF-alkoxide complexes. Similiar values have been obtained for cyclopentadienyl and silylamide complexes [16, 217].

Despite there being an obvious trend to enlargement of the Ln-OR bond lengths by increasing the coordination number at the metal center, the Ln-OR contacts seem to be particularly sensitive to the type of additional counterions as illustrated for early (Nd) and late (Y) lanthanide elements (Tables 15, 16).

Another question arose as to whether only steric factors direct the Ln-O-R bond in a bent or linear manner. In *d*-transition metal chemistry large M-O-C (alkoxide) angles are associated with π-donation of the oxygen onto the metal [218]. Consequently, covalent bond contributions are reflected in the coordination geometries adopted by the alkoxide ligands. For example, mononuclear 6-coordinate complexes of type $Ln(OR)_3L_3$ prefer the *fac*-octahedral configuration, although the *mer* arrangement should be favored for sterical reasons (Fig. 34). The fac orientation which minimizes orbital competition for oxygen-to-metal π-donation ($O(p\pi) \rightarrow Ln(d\pi)$) implies two different ligand types, one

Table 15. Mononeodymium alkoxides

Complex	CN	Ln–OR$_{av}$ [Å]	Ln-O-C [°]	Ref.
$Nd(tritox)_3(NCCH_3)_2$	5	2.162(5)	167.5(5), 171.7(5), 171.8(5)	[38]
$Nd(OC\mathit{t}Bu_2CH_2PMe_2)_3$	6	2.174(2)	–	[119]
$(CpCH_2CH_2NMe_2)_2Nd(silox)$	8	2.179(2)	167.6(2)	[207]
$Cp^{\ddagger}_2Nd[O(CH_2)_4C_5Me_5](THF)$	8	2.114(3)	–	[203]
$Cp_2Nd(OC_6H_3Ph_2\text{-}2,6)(THF)_2$	9	2.239(8)	180	[200]

Table 16. Monoyttrium alkoxides

Complex	CN	Ln–OR$_{av}$ [Å]	Ln-O-C(Si) [°]	Ref.
$Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)_3$	3	2.00(1)	171(1), 173(1), 175(1)	[63]
$Y(OSi\mathit{t}Bu_2\text{-}C_6H_4\text{-}2\text{-}CH_2NMe_2)[N(SiMe_3)_2]_2$	4	2.093(7)	141.2(4)	[129]
$Y(OSiPh_3)_3(OP\mathit{n}Bu_3)_2$	5	2.123(3)	157.8(2), 158.1(2), 174.6(2)	[47]
$Y[OSi\mathit{t}Bu_2(CH_2)_3NMe_2]_3$	5	2.097(8)	159.5(4), 164.3(5), 175.1(4)	[118]
$Cp^*Y(OC_6H_3\mathit{t}Bu_2\text{-}2,6)_2{}^a$	6	2.078(4)	128.6(3), 168.0(3)	[210]
$Y(OC\mathit{t}Bu_2CH_2PMe_2)_3$	6	2.090(4)	–	[119]
$Y(OSiPh_3)_3(THF)_3$	6	2.13(2)	168(1), 172(1), 174(1)	[47]
$Y(hftb)_3(THF)_3$	6	2.10(1)	159(1), 168(1), 174(1)	[78]
$Y(hftb)_3(diglyme)$	6	2.07(2)	159(2), 160(2), 171(1)	[78]
$[Y(OSiPh_3)_4(\eta^2\text{-}DME)][K(DME)]$	6	2.161(5)	163.7(3), 167.6(3), 168.6(3), 175.1(3)	[47]
$[Y(O\mathit{t}Bu)(Cl)(THF)_5][BPh_4]$	7	2.026(4)	179.0(1)	[45]

[a] Considering one close Y ⋯ C contact as full coordination site

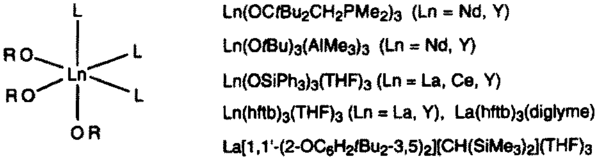


Fig. 34. Preferred *fac*-octahedral arrangement of the ligands in $Ln(OR)_3L_3$ complexes

being a significantly stronger π-donor [78]. In addition, the bridging tendency of similarly sized alkoxide ligands depends on the basicity of the alkoxide O-atom as pointed out in previous sections.

Nevertheless, the interplay thermodynamic stability and kinetic lability of the Ln-O(alkoxide) bond proved to be useful in tailoring the synthetic and catalytic reactivity of metal complexes. This section will again take up the central theme of the article and put the main emphasis on monolanthanide species.

6.1 Alkylation Reactions

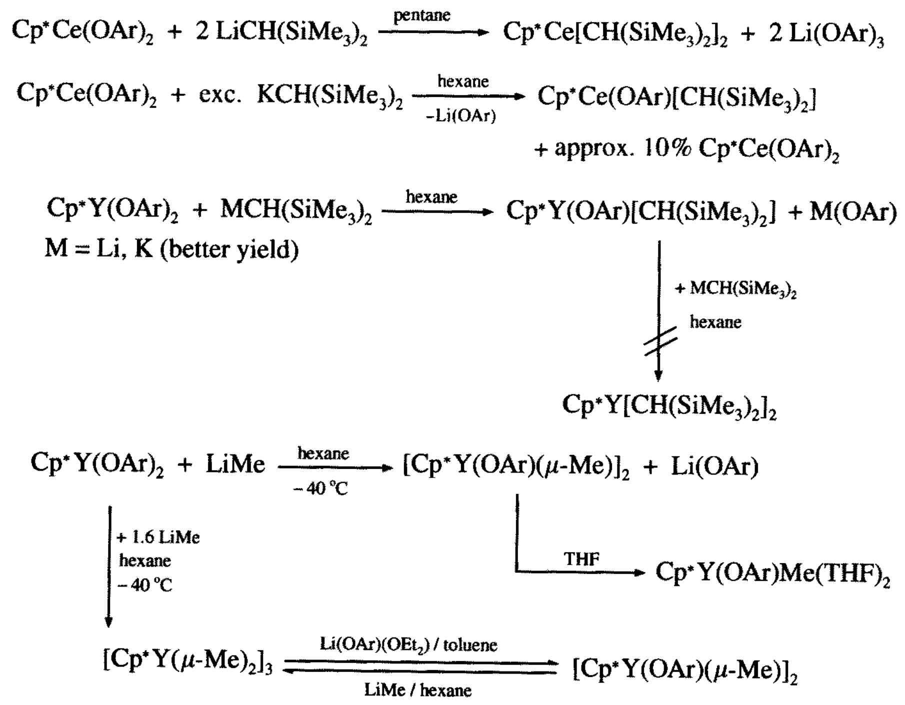
Alkoxide complexes present an attractive target for the generation of highly reactive Ln-(alkyl) bonds. Alkylation reactions impressively utilize the kinetic flexibility of the alkoxide complexes and often denucleation of the alkoxide precursor by Lewis acid-base reactions occurs. Together with the structural features worked out in the foregoing sections, the following reaction patterns should provide the essential background to deal with catalytic transformations. The reactivity of lanthanide alkoxides towards protic reagents, as well their tendency to form adduct and heterometallic alkoxide complexes, was reviewed recently [4,14] and pointed out in this article.

The first neutral homoleptic metal(III) alkyls were prepared according to the "aryloxide route" (Eq. 22) [219].

$$\begin{aligned} &\mathrm{Ln(OAr)_3 + 3\ LiCH(SiMe_3)_2} \\ &\xrightarrow{\text{pentane}} \mathrm{Ln[CH(SiMe_3)_2]_3 + 3\ Li(OAr)_3}\downarrow \quad \mathrm{Ln = La, Sm} \end{aligned} \qquad (22)$$

Precipitation of the hydrocarbon insoluble Li-aryloxide was ascribed the driving force. However, this type of kinetically controlled metathesis reaction is very sensitive to alterations of reaction conditions.

The reactivity of heteroleptic unsolvated monocyclopentadienyl complexes of type $\mathrm{Cp^*Ln(OAr)_2}$ towards alkali alkyls was studied in detail (Scheme 20) [209, 210, 220]. For $\mathrm{Cp^*Ce(OAr)_2}$ slow and solvent dependent disproportionation to $\mathrm{Cp_2^*Ce(OAr)}$ and $\mathrm{Ce(OAr)_3}$ was observed. Dialkylation is straightfor-



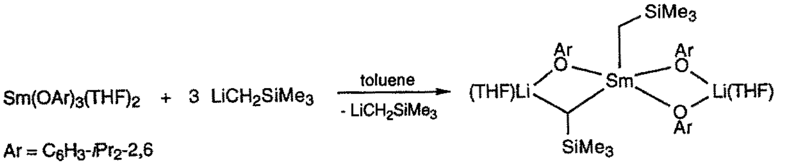
Scheme 20. Alkylation of cyclopentadienyl ligand supported aryloxide complexes

ward, employing both the larger lanthanide elements cerium and lanthanum and $LiCH(SiMe_3)_2$. $Cp^*Ce[CH(SiMe_3)_2]_2$ thermolyses at ambient temperature to $CH_2(SiMe_3)_2$ and a complex mixture of organocerium species. Even use of excess of the potassium alkyl yielded only incomplete monoalkylation with cerium derivative [209]. The yttrium aryloxide was not susceptible to dialkylation, neither with the lithium nor the potassium reagent. However, in the case of yttrium, clean and selective monoalkylation was possible and $KCH(SiMe_3)_2$ afforded better yield than $LiCH(SiMe_3)_2$. The monoalkylated products are synthetic precursors to catalytically active hydride species (Sect. 6.2.2). Use of other alkyls LiR (R = Et, *n*Bu, CH_2SiMe_3, CH_2tBu) resulted in decomposition of the starting material and formation of LiOAr. Surprising was the reaction of $Cp^*Y(OAr)_2$ with LiMe. Dimeric $[Cp^*Y(OAr)(\mu\text{-}Me)]_2$ is readily formed and the methyl bridges are cleaved by THF. Excess alkali alkyl affords dialkylation and, depending on the solvent, the reaction is reversible [220].

Alkylation of the heteroleptic CHdo-alkoxide $Y[OSitBu(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2](OC_6H_3tBu_2\text{-}2,6)_2$ with $LiCH_2SiMe_3$ led to elimination of one equivalent LiOAr (Eq. 23). The chelating siloxide ligand remains untouched, behaving as a real spectator ligand [128].

$$\begin{aligned}&Y[OSitBuAr_2][OC_6H_3tBu_2\text{-}2,6]_2 + 2\ LiCH_2SiMe_3\\&\xrightarrow{\text{toluene}} \{Y[OSitBuAr_2][OC_6H_3tBu_2\text{-}2,6][CH_2SiMe_3]_2\}^- Li^+\\&\qquad + Li(OC_6H_3tBu_2\text{-}2,6) \qquad\qquad (23)\\&Ar = o\text{-}C_6H_4(CH_2NMe_2)\end{aligned}$$

Putative $Sm(CH_2SiMe_3)_3(THF)_x$ could not be obtained from the $Sm(OC_6H_3iPr_2\text{-}2,6)_3(THF)_2/LiCH_2SiMe_3$/toluene-system [221]. Instead, complex $[Li(THF)]_2[Sm(OC_6H_3iPr_2\text{-}2,6)_3(CH_2SiMe_3)_2]$, formally derived from the addition of two equivalents of $LiCH_2SiMe_3$, was obtained (Eq. 24, Table 17). Only one OAr/alkyl exchange occurred with all aryloxide still present in the coordination sphere now occupying bridging positions. The different outcome was ascribed to sterically less bulky *i*Pr groups, THF ligation and the enhanced stability of lithium 2,6-di(isopropyl)aryloxide in toluene.

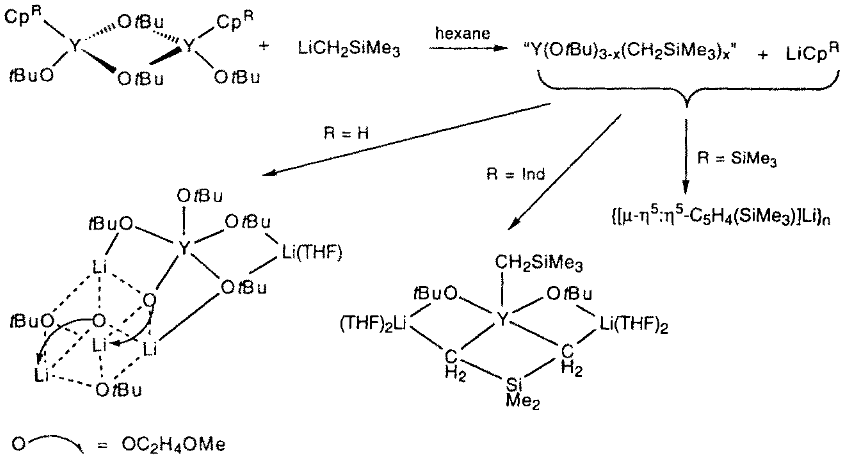


(24)

Alkyl/alkoxide metathesis employing O*t*Bu as alkoxide component revealed to be even more complicated and unpredictable [222–224]. The reactivity of well-characterized "$(CpR)_{3-x}Ln(OtBu)_x$" species towards alkali metal alkyls seems to be quite sensitive to specific reaction conditions, including choice of solvent, number and type of cyclopentadienyl co-ligands or reaction temperature.

Table 17. Alkylated lanthanide alkoxide complexes

Complex	Ln–O (alkoxide) [Å]	Ln-C	Ref.
$Y[(\mu\text{-O}t\text{Bu})AlMe_2(\mu\text{-Me})]_3$	2.21(1)	2.69(3)	[225]
$Nd[(\mu\text{-O}t\text{Bu})AlMe_2(\mu\text{-Me})]_3$	2.303(7)	2.78(1)	[226]
$Y[(\mu\text{-O}t\text{Bu})AlMe_2(\mu\text{-Me})]_2(\text{O}t\text{Bu})(THF)$	bridg. av. 2.254(6), term. 2.005(4)	2.67(1), 2.735(6)	[225]
$(CpSiMe_3)Y[(\mu\text{-O}t\text{Bu})AlMe_2(\mu\text{-Me})]_2$	av. 2.27(1)	2.562(6), 2.577(7)	[224]
$[Sm(OC_6H_3i\text{Pr}_2\text{-}2,6)_3(CH_2SiMe_3)_2][Li(THF)]_2$	2.246(6), 2.257(6), 2.294(7)	2.45(1), 2.56(1)	[221]
$[Y(CH_2SiMe_3)(\mu\text{-O}t\text{Bu})_2(\mu\text{-}(CH_2)_2SiMe_2)][Li(THF)_2]_2$	2.174(4), 2.192(4)	2.450(8)	[224]



Scheme 21. Structural evidence for Cp/Alkyl exchange in OtBu-derivatives

Expected alkoxide/alkyl exchange took place by reacting $Cp_2SmOt\text{Bu}$ with $LiCH_2SiMe_3$ according Eq. (25) [222].

$$Cp_2Sm(\text{O}t\text{Bu}) + LiCH_2SiMe_3 \xrightarrow[-78\,^{\circ}\text{C}]{\text{toluene/THF}} Cp_2SmCH_2SiMe_3 + Li(\text{O}t\text{Bu}) \tag{25}$$

Structurally characterized monocyclopentadienyl complexes $[(CpR)Y(\mu\text{-O}t\text{Bu})(\text{O}t\text{Bu})]_2$ with CpR = Cp*, Ind, $SiMe_3Cp$, MeCp, Cp were examined [223, 224]. No reaction occurred by employing the sterically saturated Cp*-complex (Scheme 21). Complexes containing the less bulky and less basic cyclopentadienyl ligands underlie immediate exchange reactions with $LiCH_2SiMe_3$ at ambient temperature. However, NMR spectra indicated the formation of cyclopentadienyl-free products of composition "$Y(\text{O}t\text{Bu})_{3-x}(CH_2SiMe_3)_x$". Loss of alkoxide ligand was not observed, neither in pentane nor toluene (Scheme 21). Despite the oily consistency of the products, crystalline material was separated off and the crystallographic data obtained unequivocally display new patterns of reactivity.

One product of the $[CpY(OtBu)_2]_2$-reaction has the composition $(OtBu)Y(\mu\text{-}OtBu)_3Li_5(\mu_3\text{-}OtBu)_2(THF)(\mu\text{-}OCH_2CH_2OMe)_2$, revealing the formation of a OCH_2CH_2OMe moiety from DME as crystallizing solvent. From the $[(CpSiMe_3)Y(OtBu)_2]$-reaction the coproduct $[Li(\mu{:}\eta^5, \eta^5\text{-}C_5H_4SiMe_3)]_n$ could be identified. Eventually, the indenyl system afforded a mixed alkyl/alkoxide monoyttrium complex. The yttrium center in $(CH_2SiMe_3)Y[(\mu\text{-}CH_2)_2SiMe_2][(\mu\text{-}OtBu)Li(THF)_2]_2$ is 5-coordinate, ligated by bridging OtBu ligands, a terminal CH_2SiMe_3 group and the two bridging methylene groups of a $(\mu\text{-}CH_2)_2SiMe_2$ moiety (Table 17) [224].

The corresponding reaction of $[(CpSiMe_3)Y(OtBu)_2]_2$ with $LiN(SiMe_3)_2$ afforded the hexane soluble monoyttrium species $Y[N(SiMe_3)_2]_3$ and $(CpSiMe_3)_2Y(OtBu)_2Li(THF)_2$ showing again loss of cyclopentadienyl along with extensive ligand restribution (Scheme 22, Table 17) [223].

A varied range of reaction products is provided by treatment of $Y_3(OtBu)_7Cl_2(THF)_2$ with the strong Lewis acid trimethylaluminum (Scheme 23, Table 17) [225]. $AlMe_3$ acts as a powerful deoligomerization reagent which simultaneously produces a kind of new chelating ligand, $[(\mu\text{-}OtBu)AlMe_2(\mu\text{-}Me)]$. A facial arrangement of the OtBu groups is observed in the "homoleptic" complex $Y[(\mu\text{-}OtBu)AlMe_2(\mu\text{-}Me)]_3$.

A steric similar situation is found in $Y[(\mu\text{-}OtBu)AlMe_2(\mu\text{-}Me)]_2(OtBu)(THF)$ where one chelating unit is replaced by a THF and a terminal OtBu ligand. Surprisingly, the chlorinated product $(OtBu)(Cl)(THF)_2Y[(\mu\text{-}OtBu)AlMe_2]$ contains both terminal OtBu and Cl ligands along with a homobridging moiety. Complexes containing such element-ligand combinations are of relevance in polymerization of conjugated dienes (Sect. 6.2.2).

Homoleptic $Ln[(\mu\text{-}OtBu)AlMe_2(\mu\text{-}Me)]_3$ (Ln = La, Pr, Nd, Y) were independently synthesized as sole products from $Ln_3(OtBu)_9$ with $AlMe_3$ (Table 17) [226]. The neodymium derivative sublimed at 100–200 °C/0.01 torr with about 50% decomposition. $AlMe_3$ is also capable of disrupting the alkoxide bridges in $[(CpSiMe_3)Y(OtBu)_2]_2$ to yield $(CpSiMe_3)Y[(\mu\text{-}OtBu)AlMe_2(\mu\text{-}Me)]_2$ (Table 17) [224].

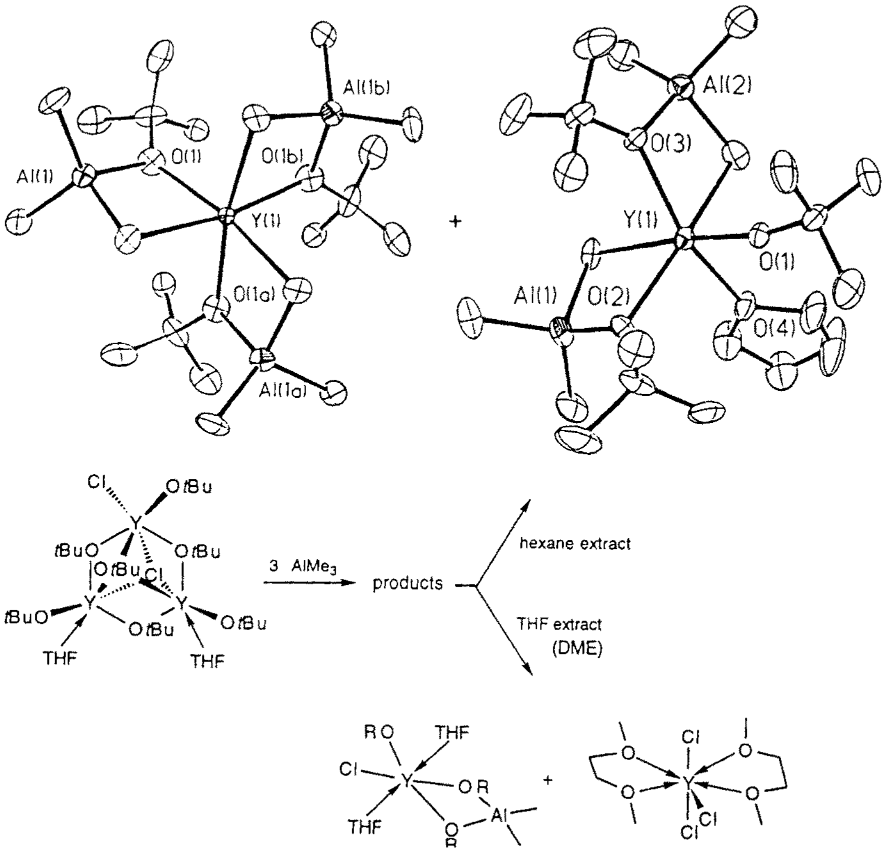
6.2 Catalytic Transformations

A major handicap to the application of lanthanide alkoxides in organic synthesis (Sect. 6.2.1) and polymerization reaction (Sect. 6.2.2) is their sensitivity

$$[(CpSiMe_3)Y(OtBu)_2]_2 + 2\ LiN(SiMe_3)_2$$

$$\xrightarrow{\text{hexane extract}} (CpSiMe_3)_2Y(OtBu)_2Li(THF)_2 + Y[N(SiMe_3)_2]_3$$

Scheme 22. Amidation of a heteroleptic yttrium alkoxide



Scheme 23. Reactivity of $AlMe_3$ with $Y_3(OtBu)_7(Cl)_2(THF)_2$ – molecular structures [225]

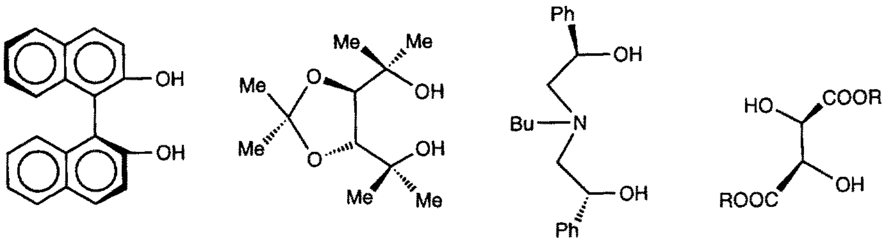
towards moisture and protic solvents. Reactions are therefore conducted in an appropriate choice of dry solvent [227]. However, structurally and electronically fine-tuning of the alkoxide ligand can produce complexes which exhibit remarkable stability against water. "Water adducts" which can be seen as the first step of hydrolysis could be isolated and structurally characterized [129]. In some cases, the presence of water even plays a key role in the way a catalytic system works [158]. The third part of this section is dedicated to the structural elucidation of relevant molecular species.

6.2.1 Organic Synthesis

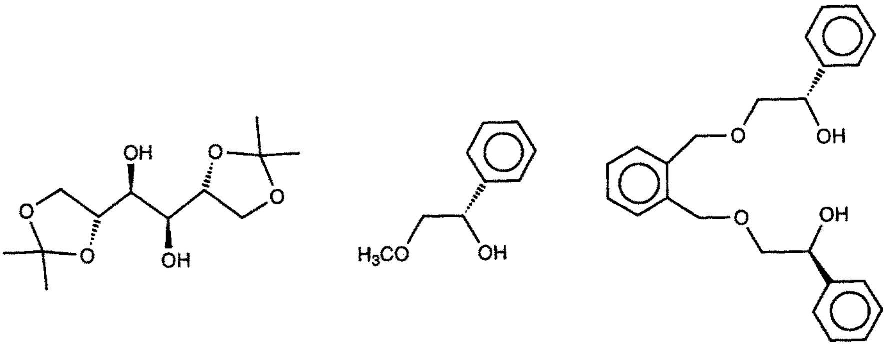
Lanthanide reagents are meanwhile well established in organic synthesis [5, 227]. While the reactivity of low valent species generally resembles that of the group IA and IIA elements, complexes of type LnR_3 show reaction patterns similar to group IIIA and the early transition d-metals Ti, V and Mo. Like other organometallic systems which contain highly polarized Ln-O-C linkages, including fluorinated β-diketonate [86] and triflate complexes [228], lanthanide alkoxides boost selective organic catalysis.

This section will give an outline of catalytic organic transformations where lanthanide alkoxides are, in particular, used as precatalysts. It must be assumed that other precatalysts underlie in situ formation of catalytically active Ln-O(alkoxide) moieties [229]. For example, in reactions involving ketones or aldehydes as substrates, enolate intermediates often act as the real active catalyst component. Many reactions are conducted in alcoholic solutions like MeOH or *t*BuOH or ethylene glycol [5]. Alcohols are often needed as proton source and their steric bulk can influence the product selectivities [230].

The readily available system "Ln(O*i*Pr)$_3$" made the running for the others in carbon-carbon bond generations and functional group modifications. Meanwhile, the steadily growing demand for stereo- and enantioselective reagents has also affected the lanthanide elements and as a result more sophisticated ligands have been introduced (Fig. 35A–G).



A ((S)-BINOL) **B** **C** **D** (L(+)-tartrate; R = Et, *i*Pr)



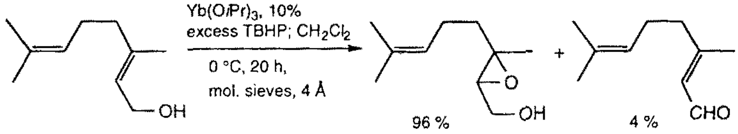
E **F** **G** (DHPEX)

Fig. 35A–G. Optically active alcohol ligands employed for Ln-catalyzed organic transformations

$Ln_5O(OiPr)_{13}$-Mediated Reactions

For the first time, catalytic activity of lanthanide isopropoxides was detected in the TBHP (*tert*-butylhydroperoxide) assisted oxidation of allylic alcohols to epoxyalcohols (Eq. 26) [231]. For example epoxy geraniol was obtained in up to 96% yield by using "$Yb(OiPr)_3$" in the presence of molecular sieves (4 Å) [232].

Catalytic ring opening of epoxides and aziridines was also observed (Eq. 27). The acetone cyanohydrine reaction provided *β*-hydroxy nitrile and *β*-amino nitriles, with the lanthanide isopropoxides exhibiting a higher reactivity than Et_3N [233].



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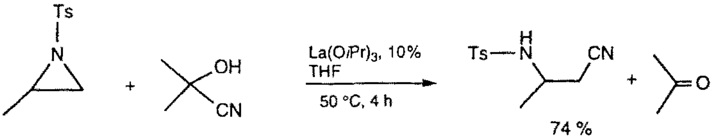
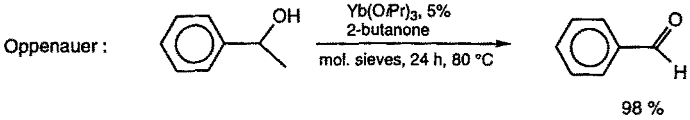


(27)

Catalytic Oppenauer oxidations (Eq. 28) and Meerwein-Ponndorf-Verley reductions (Eq. 29) were studied in detail [232, 234]. The gadolinium derivative, employed in situ without elimination of LiCl, was reported to be ten times more reactive in the MPV reduction of cyclohexanone as the standard reagent $Al(OiPr)_3$ [235].



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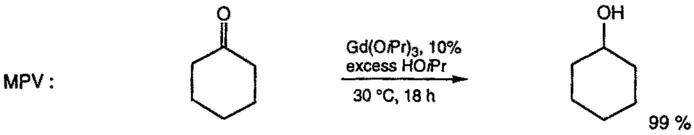
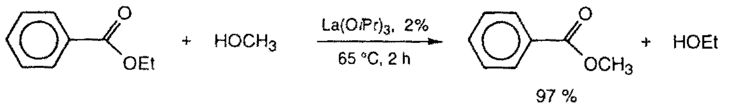


(29)

Transesterification [236] and the ester exchange reaction [237] were reported to be efficiently catalyzed (Eqs. 30 and 31). Either of the exchange reactions are sensitive to steric constraints of the substrates and to metal ion size. For example, transesterification is most applicable to primary alcohols. Increased catalytic activity in the presence of larger lanthanide centers is explained by enhanced coordinative unsaturation and increased basicity of the alkoxide complexes. Strong basicity of the lanthanide isopropoxides is considered to catalyze effectively the transhydrocyanation from acetone cyanohydrin to several aldehydes and ketones (Eq. 32) [238]. "$YbBu_3$" exhibited similar catalytic activity in this reaction.



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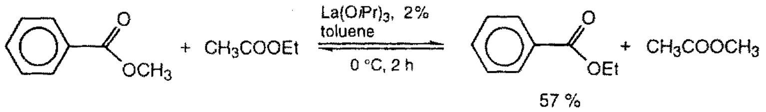

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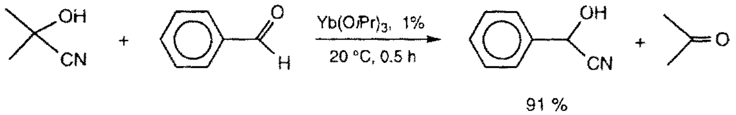


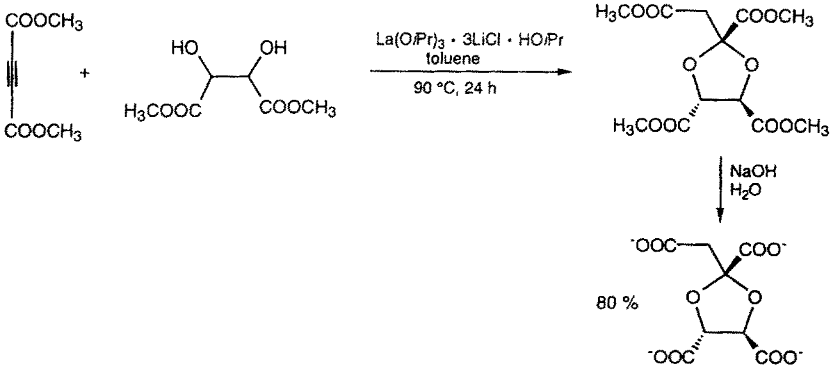
(32)

Lanthanide(III) isopropoxides catalyze the addition of hydroxyl compounds to unsaturated carboxylic acids (Scheme 24) [239]. The resulting ethercarboxylates can be used as metal sequestrants and are, in general, readily biodegradable. Other Ln(III) reagents such as $LnCl_3$ or Ln_2O_3 also mediate these Michael-type reactions [240]. However, the high basicity of the alkoxide solutions decisively enhance the conversion.

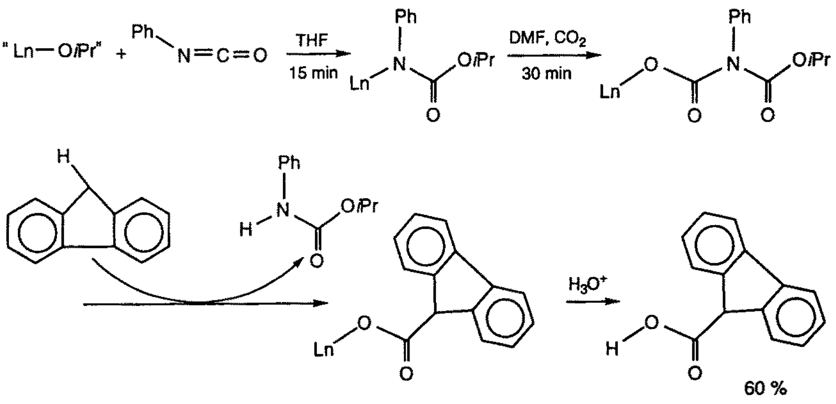
Insertion complexes of lanthanide isopropoxides with isocyanate can act as carbon dioxide carrier for the carboxylation of "active methylene compounds", as exemplified in Scheme 25 [241]. The catalytic formation of urethane is based on insertion of isocyanate into the La-O*t*Bu bond of $La_3(OtBu)_9(THF)_2$ [242].

Heteroleptic Alkoxides

Iodo alkoxides, which were prepared according Eqs. (33) and (34), also revealed promising activity in MPV-Oppenauer reactions [243], but did not reach the activity of SmI_2 [229]. A cooperative effect of the basic alkoxide oxygen, the soft



Scheme 24. Michael-type formation of ethercarboxylates

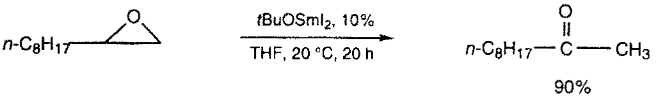


Scheme 25. Lanthanide isopropoxides involved in carbon dioxide transport

nucleophile I^- and the Lewis acidic Ln^{3+} center was made responsible for the selectively catalyzed rearrangement of terminal epoxides to methyl ketones by tBuO-LnI_2 (Eq. 35) [244a]. However, the latter complex afforded better regioselectivities in ring opening reactions of epoxides compared to $SmI_2(THF)_2$ [244b]. Silylated nucleophiles as trimethylsilylcyanide are assumed to attack preferably on the less hindered side of styrene oxide due to the bulky *tert*-butoxide group of the precatalyst (Eq. 36).

$$2\ SmI_2 \quad + \quad tBuOOtBu \quad \xrightarrow{THF} \quad 2\ tBuOSmI_2 \qquad (33)$$

$$Ce \quad + \quad I_2 \quad + \quad HOiPr \quad \longrightarrow \quad iPrOCeI_2 \quad + \quad 0.5\ H_2 \qquad (34)$$



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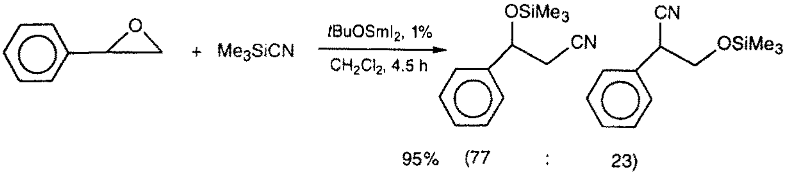


(36)

Type and geometry of substrate coordiation plays a key role in the final stereochemistry of the product [245, 246]. Organolanthanide catalyzed condensation of carbonyl compounds with silylenolethers, known as the Mukaiyama addition reaction, is assumed to contain a 6-membered transition state with Ln-O linkages [247]. Formation of a 6-membered organolanthanide aldolate moiety was structurally proven in the reaction of Cp^*_2 LnR with ketones (Sect. 6.2.3) [248].

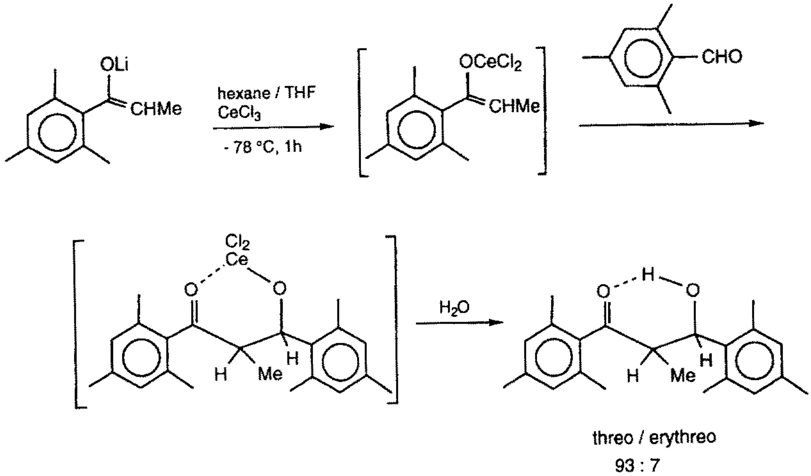
Cerium enolate complexes of type $Cl_2Ce(OCR{=}CHR)$ achieve higher yields in stoichiometric cross-aldol reactions of sterically crowded substrates than the corresponding lithium enolates (Scheme 26). The larger cerium is assumed to be more effective in the inital aldol chelate formation. Formation of α-bromo-β-hydroxyketones is also catalyzed [249].

Enantioselective Reactions

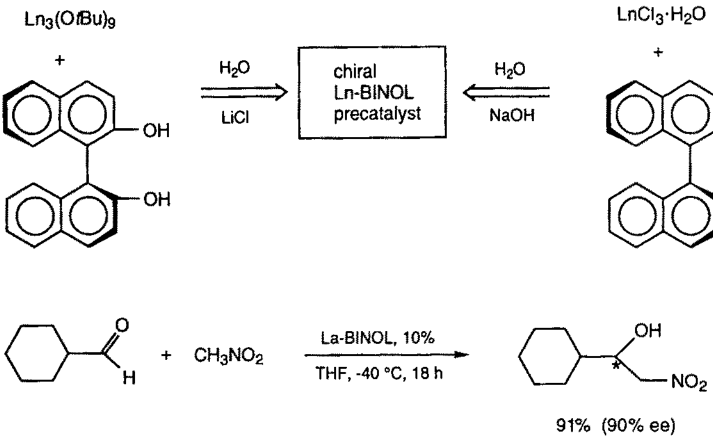
Stereoselective formation of carbon carbon and carbon heteroatom bonds remains an important goal in synthetic chemistry. Very recently lanthanide alkoxides were successfully utilized in enantioselective C-C bond forming reactions. Catalysis of aldol, cyanosilylation, nitroaldol and Michael reactions has been ascribed to the basic character of lanthanide alkoxides [158, 250, 251]. $Ln_3(OtBu)_9$ was successfully employed in test runs and subsequently optically active bidentate ligands were used (Fig. 35) [250a].

Strongly chelating ligands provide a sterically rigid ligand frame, a prerequisite for induction of asymmetry at the lanthanide center. Complexes derived from (S)-(−)-BINOL were thoroughly studied in the nitroaldol reaction (Henry reaction, Scheme 27) [250].

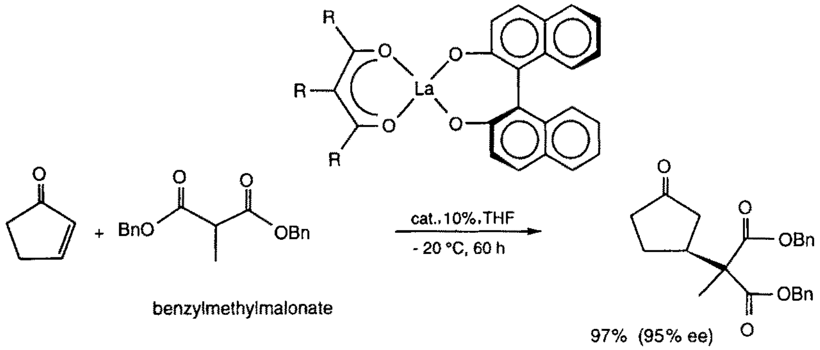
The presence of LiCl and H_2O is essential for both acceleration of the reaction rate and enhancement of the enantiomeric selectivity. Typical substrate/catalyst compositions are in the ratio substrate : Ln-BINOL : LiCl : H_2O = 10 : 1 : 2 : 10 [250b]. Light could be thrown on the catalyst structure by examination of the sodium derived species as $Na_3Ln[(S)\text{-BINOL}]_3 \cdot 6THF \cdot 2H_2O$ (Sect. 4.2) [158]. However, the nitroaldols obtained from the sodium derivatives were mostly racemic which once more emphasizes the importance of LiCl. It was also found that larger lanthanide elements gave both higher chemical and optical yields



Scheme 26. Cross aldol reaction mediated by a cerium enolate complex



Scheme 27. Catalytic asymmetric nitroaldol reaction

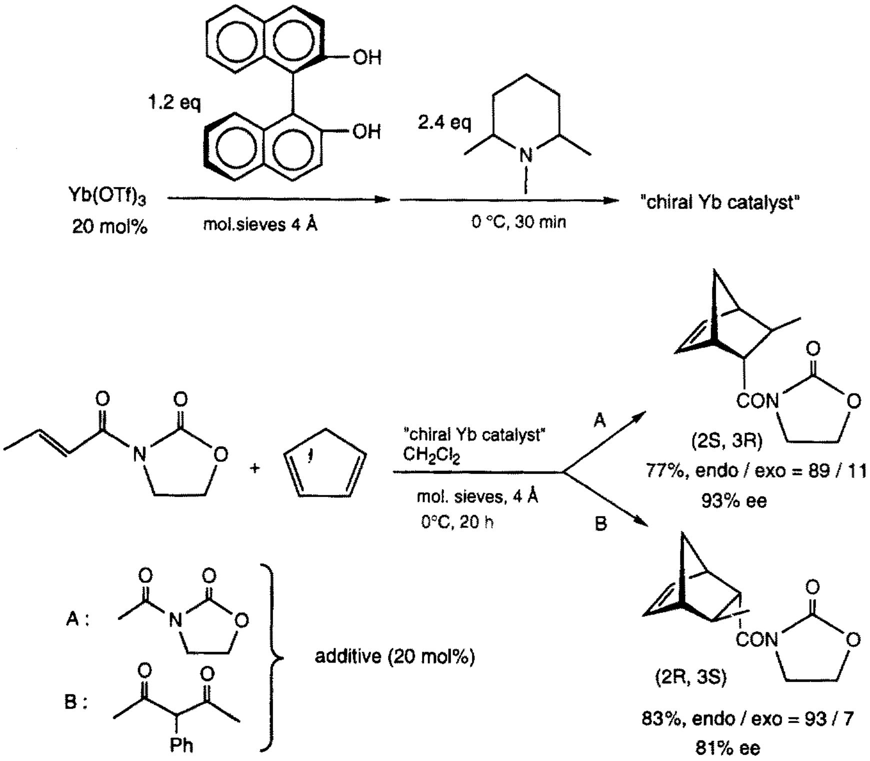


Scheme 28. Catalytic asymmetric Michael reaction

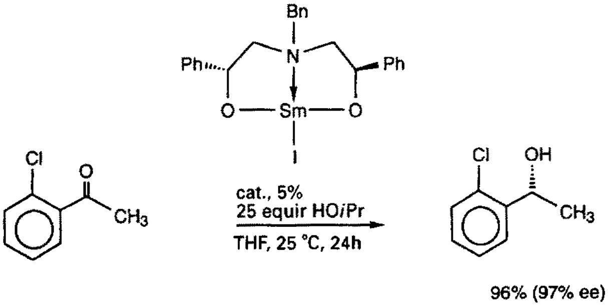
[250d]. A yttrium derivative of another optically active ligand (Fig. 35B) was less effective [250a].

In contrast, asymmetric Michael reactions are promoted by alkali metal free La-BINOL ester enolate complexes (Scheme 28) [251]. The catalyst is best prepared by successive addition of the Michael donor and (S)-BINOL to $La(O\textit{i}Pr)_3$.

The (R)-(+)-BINOL ligand afforded chiral ytterbium and scandium triflates according to Scheme 29 which proved to be good catalysts in asymmetric Diels-Alder reactions of some dienophiles with cyclopentadiene. The enantioselectivity could be controlled by achiral dienophile additives [252]. IR-spectroscopic examinations of the precatalyst system indicated hydrogen bonds between the phenolic hydrogens of the BINOL ligand and the nitrogens of the tertiary amines. Such transfer of axial chirality to the amine part is consistent with the observation that bulkier amines gave better selectivities.



Scheme 29. Catalytic asymmetric Diels Alder reaction



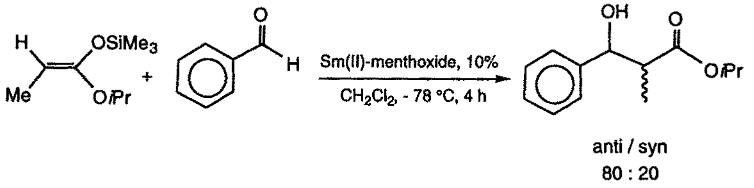
Scheme 30. Catalytic asymmetric MPV reduction

Chiral induction was also observed in lanthanide(III)-alkoxide-mediated MPV reductions. The optically active ligand (Fig. 35C) was used in enantioselective samarium-catalyzed MPV reductions of arylmethyl ketones (Scheme 30) [253]. The resulting mixed alkoxide-iodide complex shows higher reactivity than (tBuO)SmI$_2$. It was pointed out that the tridentate, secondary alkoxide ligand is not oxidized under the reaction conditions and that tridendate ligands afford higher enantioselectivities than bidendate ligands. Alkyl substitution of the carbonyl C-atom, alcohol hydride source and size of the lanthanide metal sensitively affect the reaction outcome. Lower enantiomeric excesses (< 32%) were reported for MPV reductions employing other chiral ligands (Fig. 35A, D and E(R = *i*Pr)) [254]. Type of in situ preparation of the lanthanide precatalyst was found to affect significantly the reactivity and enantiomeric excess. A determining effect, even though a rather unpredictable one, was ascribed to the Ln(III) ion size.

Chiral CHdo-alcohols (Fig. 35D (R = Et), F and G) as proton source mediate the enantioselective protonation of Sm-enolates according to Scheme 31 [255]. The optimal molar ratio of DHPEX (Fig. 35G) and HMPA were about 0.7 and 0.6, respectively. Steric factors dominate the enantioselectivity of this reaction sequence when unsymmetrical dialkylketenes are used. High enantiomeric excesses were achieved when the difference between the bulkiness of the alkyl groups for a given substrate is large. The relationship between the enantioselectivity of the protonation and the E/Z selectivity of Sm-enolate formation which is dependent on type of alkyl substitiution was examined.

Lanthanide(II) Reagents

Alkoxide ligands may also provide an alternative ligand set in widely used Ln(II) compounds [256]. Enolate and aldolate complexes of type $X_2Ln(III)$-OR or XLn(II)-OR are often assumed intermediates in $Ln(II)X_2$ and XLn(II)R (R = alkyl) promoted reactions with carbonyl compounds [257]. In addition, structural investigations support the fact that strongly reducing Sm(II) can be stabilized in sole oxygen environment (Sect. 2.3) [74, 75]. Preliminary catalytic investigations revealed that Sm(II) menthoxide and O-1-adamantoxide are stable under aldol reaction conditions and catalyze the reaction of silyl ketene acetals with aldehydes (Eq. 37) [258].



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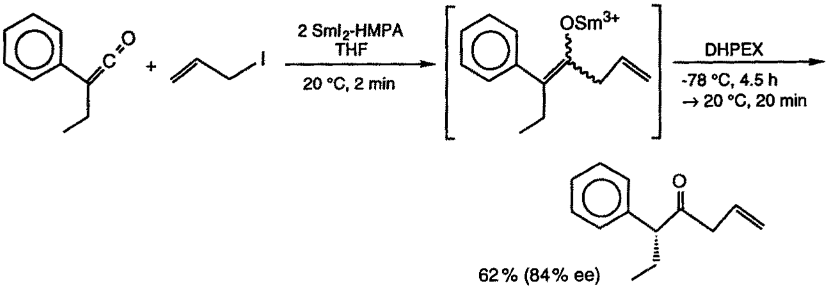
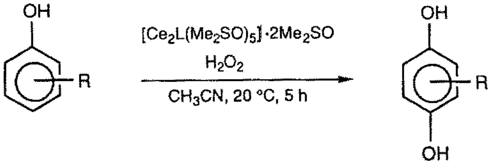


Scheme 31. Enantioselective protonation of Sm-enolates

Interestingly, better diastereoselectivity is obtained than in the corresponding reactions with trivalent lanthanide alkoxides. The use of optically active (L)-menthoxide afforded moderate enantioselectivities. Further stimulus for "Sm(II)-OR"-based transformations has come from the initial investigations of Sm(II)-triflate mediated Grignard-type reactions [259].

Cerium (IV) Reagents

A homobimetallic cerium(IV)-calix[8]arene complex was used together with hydrogen peroxide in the regioselective hydroxylation of simple phenols (Eq. 38). Just 0.5 mol of the cerium complex was sufficient to convert 1 mol phenolic substrate [260].



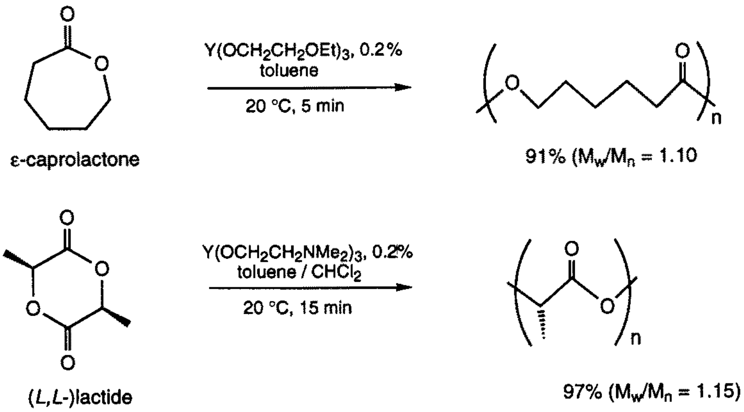
(38)

H_8L = *p-tert*-butylcalix(8)arene

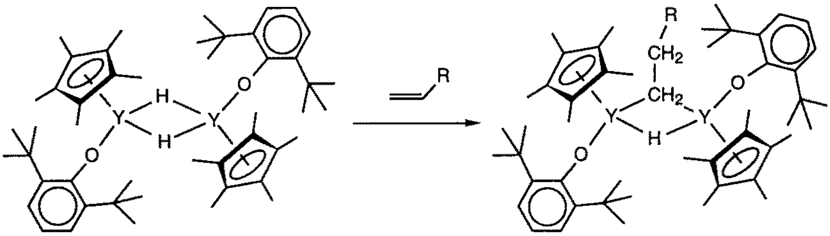
6.2.2 Polymerization Reactions

Binary systems of the Ziegler Natta type containing rare earth components are known as effective catalysts in butadiene, acetylene and co-polymerization reactions [261]. Alcoholate and alkoxide systems of type $LnCl_3(HOR)/AlR_3$ and $Nd(OiPr)_{3-n}Cl_n/AlR_3$, respectively, show high activity and stereospecificity. It was shown that the counterion bounded to the lanthanide center has a remarkable effect both on the rate of polymerization and the stereospecificity. For example, $NdCl(OCOCF_3)_2$ gave 98.5% *cis* 1,4- and $Nd(OCH_2tBu)_3$ gave 95% *trans* 1,4-polybutadiene [262].

Yttrium(III) isopropoxide and $Y(OCH_2CH_2OEt)_3$ initiate rapid living ring-opening polymerization of ε-caprolactone at ambient temperature (Scheme 32) [263]. Reactions are complete in less than 5 min, exhibiting low polydispersities ($M_w/M_n < 1.2$). $La_5O(OiPr)_{13}$ causes rapid polymerization even at −64 °C. Biodigradable polylactide was obtained from (L, L)-lactide with CHdo-alkoxides of type "$Ln(OCH_2CH_2NMe_2)_3$" as effective catalysts (Scheme 32) [264]. Again, living ring opening polymerization was established by observation of low polydispersity (< 1.2) at high conversion and linear increase of molecular weight with conversion. The reaction is zero order in monomer and the turnover frequency for $Y(OCH_2CH_2NMe_2)_3$ in CH_2Cl_2 at ambient temperature is estimated at 30 min^{-1}. Again the lanthanum derivative is even more reactive. For comparison, the fastest aluminum alkoxide initiator $Al(OiPr)_3$ is reported at 0.78 min^{-1} at 70 °C and 1.3 mol l^{-1} lactide. AB block copolymers could be obtained by sequential addition of (L, L)-lactide and (D, D)-lactide (M_w/M_n = 1.38) as well as ε-caprolactone and (L, L)-lactide monomers (M_w/M_n = 1.36).



Scheme 32. Ringopening polymerization of lactones by CHdo-alkoxides



Scheme 33. Olefin insertion into an Y-H bond in the presence of an aryloxide co-ligand

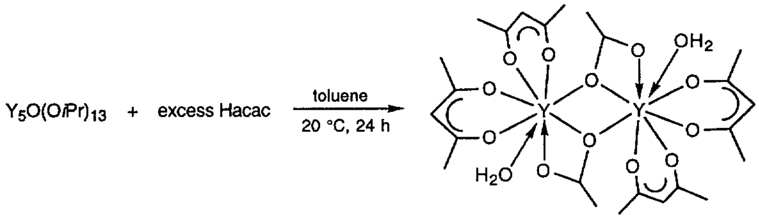
Organolanthanide complexes with alkoxide co-ligands were also tested as catalysts in homogeneous α-olefin polymerization [220, 221, 265]. The alkoxide ligand in $[Cp^*Y(OC_6H_3tBu_2\text{-}2,6)(\mu\text{-}H)]_2$ changes the steric and electronic situation at the metal center compared to well-examined "Cp_2LnH" species [266]. It was found that terminal olefins $H_2C = CHR$ (R = H, Me, Et, *n*Bu) insert regiospecifically and irreversibly into one μ-H bond to yield a μ-*n*-alkyl species with *trans* geometry for the ancillary ligands (Scheme 33). Allyl species analogous as in the "Cp_2^*YH"- reaction are not observed. These compounds polymerize ethene and behave as single-component catalysts for the polymerization of α-olefins and nonconjugated dienes. The aryloxide ligands stabilize longer chain alkyl bridges, e.g., $\mu\text{-}nC_6H_{13}$, with respect to β-elimination. Terminal acetylenes as $HC \equiv CSiMe_3$ give protonolysis with loss of H_2 and slow dimerization to the head-to-head enyne *trans*-$Me_3SiCH{=}CHC{\equiv}CSiMe_3$.

6.2.3 Catalyst Structure

Structural elucidation of catalytically active species and reaction intermediates is important for understanding the catalyst reactivity and for assisting in further developments, e.g., synthesis of more effective catalysts by tuning of the ligand sphere.

While the structural composition of some precatalysts like $Ln_5O(O\textit{i}Pr)_{13}$ [9], $Ln_3(O\textit{t}Bu)_9$ [10], $Na_3Ln(BINOL)_3 \cdot 6THF \cdot 2H_2O$ [158] is well known, the identification of alkoxide species involved in selective organic transformations is often complicated and hence scarce. Even precatalysts are usually prepared in situ without further isolation or separation and often the outcome of the catalyzed process depends markedly on the presence of coproducts. At this point, and because of the scarceness of detailed data on "active catalyst structure", the author also wants to consider well-characterized species which contain relevant alkoxide moieties. Corresponding complexes usually result from reactions of organolanthanides with carbonyl compounds [267–270]. This consideration should not only spur the organic chemists to shed more light on their functioning "catalytic systems". Screening of the "black box" is desirable not only for reasons of process optimization. Unforeseen reactions of highly reactive organolanthanide catalysts under the prevailing reaction and storage conditions are known to occur even in the absence of substrate. Cleavage of ether solvents has already been mentioned in an earlier section [202, 203, 205]. Scheme 34 once again summarizes several of these accidental reactions as ether cleavage [271–273], carbon dioxide insertion [206], partial hydrolysis [274, 275] and cluster formation [51].

Unexpected cleavage of acetylacetone occurred when slowly adding excess of Hacac to a solution of $Y_5O(O\textit{i}Pr)_{13}$ (Eq. 39) [276]. The formation of an acetato moiety could be explained in terms of a retro-Claisen condensation.



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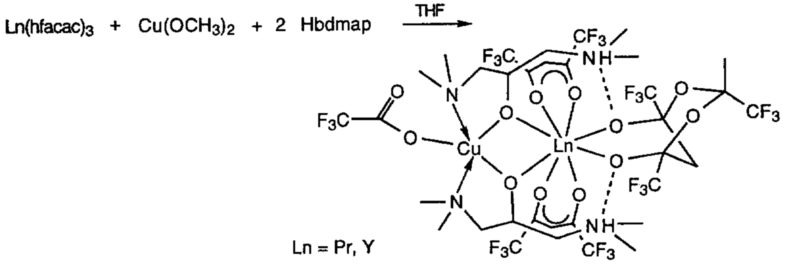
Both the acetate and acetone components of the suggested reaction sequence could be trapped in a side product during the preparation of a mixed ligand/metal complex according to Eq. (40) (Table 18) [140].



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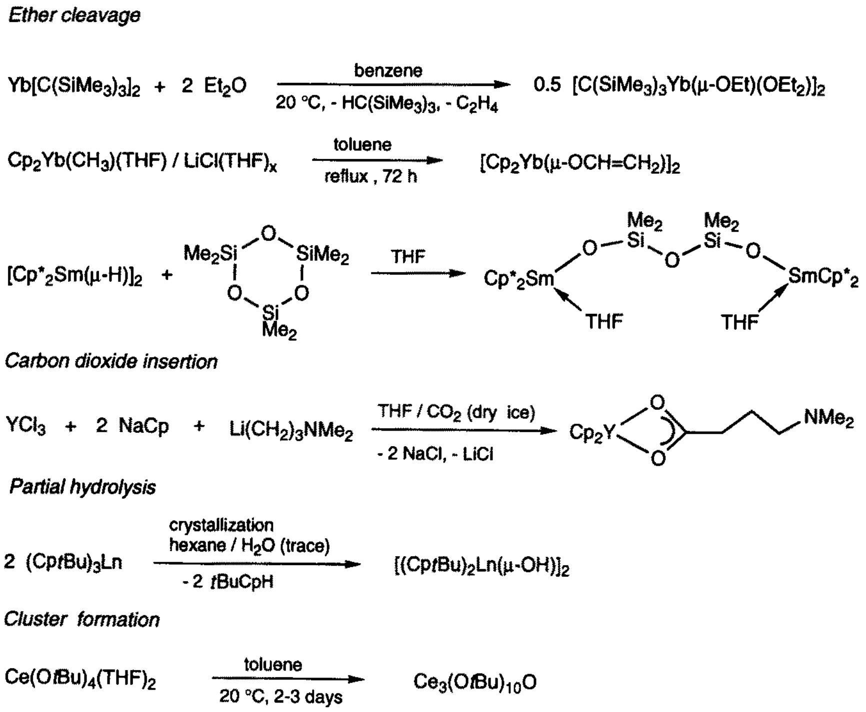


Scheme 34. Accidental Ln-O(R) bond formations

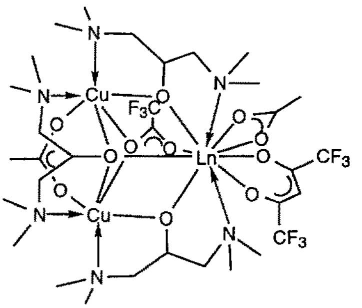
Table 18. Lanthanide complexes containing terminal Ln-alkoxide bonds

Complex	Ln–O [Å]	Ref.
$[Cp^*_2Sm(THF)]_2(\mu\text{-}OSiMe_2OSiMe_2O)$	2.157(5)	[272b]
$PrCu(Hbdmap)_2(hfacac)_2(O_2CCF_3)L$ [a]	2.39(1) – 2.46(1)	[140]
$NdCu_2(bdmap)_3(hfacac)(O_2CCH_3)(O_2CCF_3)$	2.36(1), 2.44(2), 2.75(1)	[140]
$[Yb(OCPh_2)_2(HMPA)_2]_2$	2.11(3), 2.39(2)	[278]
$Sm(OC_6H_3t\text{Bu}_2\text{-}2,6\text{-}Me\text{-}4)[OC(=C_6H_4)Ph]_2(HMPA)_2$	aryloxide: 2.187(8) enolate: 2.170(11), 2.189(13)	[279]
$Sm(OC_6H_3t\text{Bu}_2\text{-}2,6)(OCHPh_2)_2(HMPA)_2$	alkoxide: av. 2.143(5)	[279]
$(Cp_2Lu)_2(O_4C_{12}H_{18})$	2.09, 2.215	[281]
cis-$[Cp^*_2Sm(Ph_3PO)]_2(\mu\text{-}OCH{=}CHO)$	2.147(19), 2.179(10)	[282]
trans-$[Cp^*_2Sm(Ph_3PO)]_2(\mu\text{-}OCH{=}CHO)$	2.122(8), 2.107(7)(disorder)	[282]
$Cp^*_2Sc[OC(CH_3)]Co(CO)Cp$	2.067(2)	[281b]
$(Cp^*_2Y)_2(\mu\text{-}\eta^2{:}\eta^2\text{-dipyridylketone})$	2.353(8), 2.356(8)	[283]
$[Cp^*_4Sm_2(O_2CCCO)(THF)]_2$	2.25(1), 2.39(1)	[284]
$[Cp^*_2Sm]_2(O_2C_{16}H_{10})$	2.08(2)	[285]
$[Cp^*_2Sm(THF)]_2(O_2C_{16}H_{10})$	2.099(9)	[280c]
$[Cp^*_2Sm]_2[\mu{:}\eta^4\text{-}(C_5H_4N)CH{=}COCO{=}CH(C_5H_4N)]$	2.191(6)	[286]
$[Cp^*_2Sm]_2[\mu{:}\eta^4\text{-}(PhN)CH{=}COCO{=}CH(NPh)]$	2.30(1)	[287]
$Cp^*_2Ce(OCMe_2CH_2COCH_3)$	2.182(4)	[248]
$Cp^*_2Sm(MMA)_2H$	2.188(9)	[289]

[a] L is shown in Eq. (40)

It has been proposed that the unusual dialkoxide ligand formed is the result of the cyclo addition of 1,1,1-trifluoro-2,2 propandiol, the hydration product of trifluoroacetone, to the hfacac ligand (Scheme 35). The retro-Claisen condensation of hfacac was probably induced by the Lewis bases 1,3-bis(dimethylamino)-2-propanol or methoxide and the presence of water. Crystallographic data reveal the formation of a zwitterionic form of the aminoalkoxide and hence support a deprotonation of the 1,1,1-trifluoro-2,2 propandiol by its Lewis basic character. Decomposition of the hfacac ligand was again crystallographically detected in the $LnCu_2$ complex prepared according to Eq. (41) (Table 18) [140].

$$\mathrm{Ln(hfacac)_3} + \mathrm{Cu_2(O_2CCH_3)_4(H_2O)_2} + 3\ \mathrm{Hbdmap} \xrightarrow[-\ \mathrm{Hhfacac},\ -\ 2\ \mathrm{HO_2CCH_3},\ -\ \mathrm{CH_3COCF_3}]{\mathrm{THF}}$$



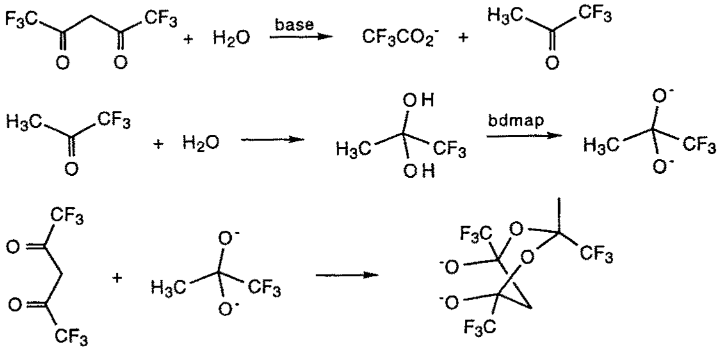
(41)

Ln = Pr, Nd

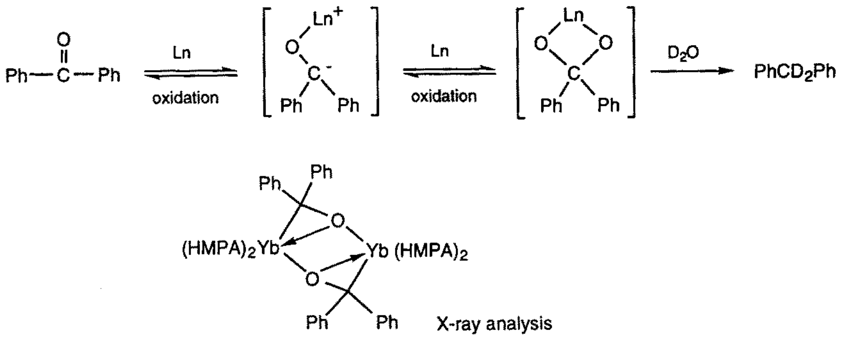
Active catalyst species or catalysis intermediates can often be trapped by stoichiometric reactions of the precatalyst with the substrate. The following example describes the successful isolation of such an intermediate with participation of Ln-O σ-bonds. Reduction processes mediated by low oxidation states of the lanthanide elements are of special interest in organic synthesis [256]. One of the most intensively studied reactions is the stoichiometric reduction of arylketones by rare earth metals ytterbium and samarium [277]. Thus formed dianions possess high nucleophilic character and excess lanthanide metal can even accomplish complete cleavage of the C-O double bond (Scheme 36).

The reaction product of ytterbium metal with benzophenone in a 1:1 molar ratio could be determined by an X-ray structure [278]. The benzophenone dianion unsymmetrically bridges the ytterbium atoms in the HMPA solvate $[Yb(OCPh_2)_2(HMPA)_2]_2$. The aryl oxygen forms a Yb-O bond with a typical terminal bond length (Table 18), but also donates to the other ytterbium. A Yb-C σ-bond involving the α-C-atom (2.59(5) Å) balances the charge at Yb (II). Reaction of the dianionic complex with four equivalents of phenol $HOC_6H_3tBu_2$-2,6-Me-4 afforded the mononuclear aryloxide complex $Yb(OAr)_2(HMPA)_2$ (Sect. 4.2) [72].

However, treatment of the analogous samarium benzophenone dianion with the phenol resulted in oxidation to a mononuclear mixed aryloxide/enolate Sm(III)-complex, $Sm[OC{=}(C_6H_6)(Ph)]_2(OAr)(HMPA)_2$, where protonation occured at the aromatic rings (Fig. 36A) [279]. The ligands are arranged in



Scheme 35. Mechanistic steps proposed for the formation of an unusual dialkoxide ligand



Scheme 36. Reduction of arylketone by Ln (Yb, Sm) metal

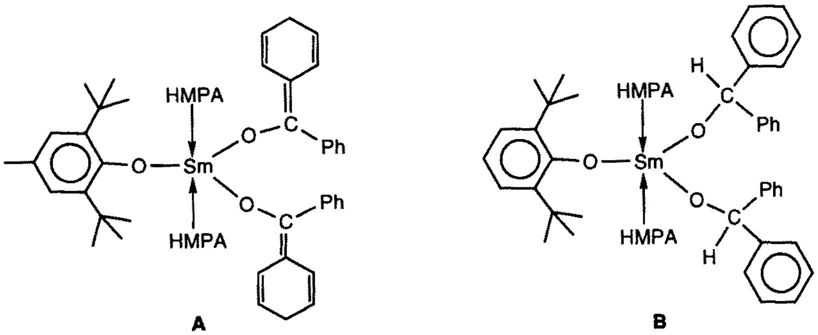


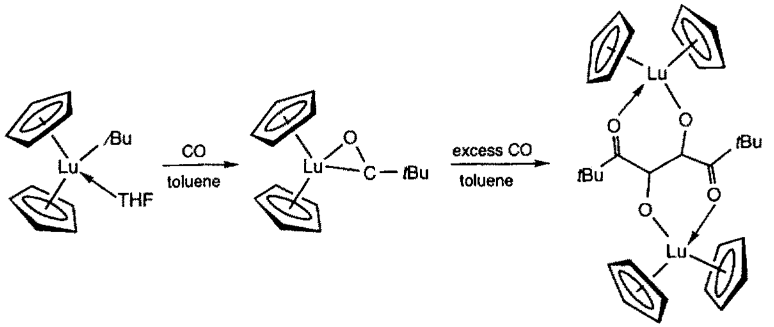
Fig. 36A, B. Mixed aryloxide/enolate Sm(III)-complexes [279]

a trigonal bipyramidal fashion around the samarium with the aryloxide and enolate ligands occupying the equatorial sites. Reaction with excess of $HOC_6H_3tBu_2$-2,6 does not result in Birch-like protonation of the enolate form, but only aryloxide exchange occurred. However, upon heating (80 °C) isomerization to the diphenylmethoxide took place (Fig. 36B). The Sm-O (alkoxide) bond lengths are shorter than the Sm-O(enolate) bond distances (Table 18).

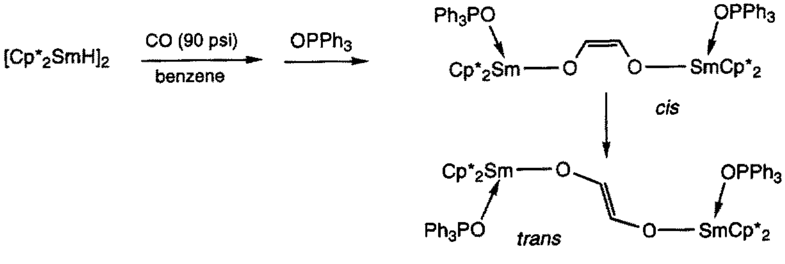
Organolanthanide compounds display a remarkable chemistry with the simplest carbonyl derivative, namely carbon monoxide [280–287]. Organolanthanide activation of carbon monoxide was first observed by employing the monomeric alkyl complex $Cp_2Lu(tBu)(THF)$ (Scheme 37) [281a]. Reaction of one equivalent CO yielded single insertion of CO into the Ln-*t*Bu bond to form a η^2-acyl complex. However, excess CO yielded a multiple insertion and coupling of four molecules of CO led to an enedione diolate moiety which bridges two lutetium atoms (Table 18).

Lanthanide hydrides of type $Cp^{\ddagger}_2SmH$ are capable of both reducing and coupling carbon monoxide (Scheme 38) [282]. The initially formed *cis* enediolate isomerizes to *trans*-$[Cp^{\ddagger}_2Sm(Ph_3pO)]_2(\mu\text{-}OCH{=}CHO)$ at ambient temperature in hours to days depending on sample concentration. The Sm-O bond of the bridging enediolate moiety is in the range of terminal Sm-O(alkoxide, enolate) bonds (Table 18).

Addition of Sc-R moieties to metal coordinated carbon monoxide was ascribed to the high Lewis acidity of the organometallic scandium complexes [281b]. R-Substituted scandoxycarbene complexes of type $Cp_2M{=}C(R)OScCp^{\ddagger}_2$ (M = Mo, W; R = H, Me) and $CpM(CO)[{=}C(R)OScCp^{\ddagger}_2]$ (M = Co, Rh, R = H, Me, CH_2CH_2Ph, NMe_2) were obtained. The molecular structure of

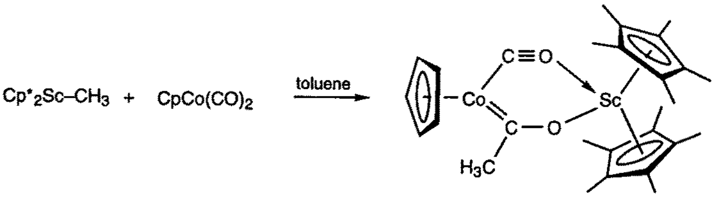


Scheme 37. CO insertion and coupling reactions mediated by a Lu-C(*t*Bu) bond



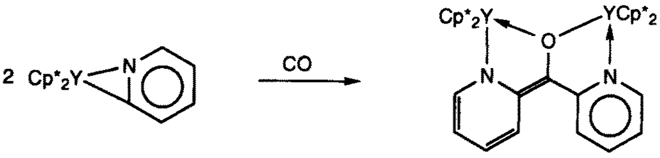
Scheme 38. CO insertion and coupling reactions mediated by a Sm-H bond

CpM(CO)[=C(R)OScCp$^*_2$] reveals a μ_2, η^1, η^1-carbonyl ligand in addition to the scandoxycarbene moiety (Eq. 42, Table 18).



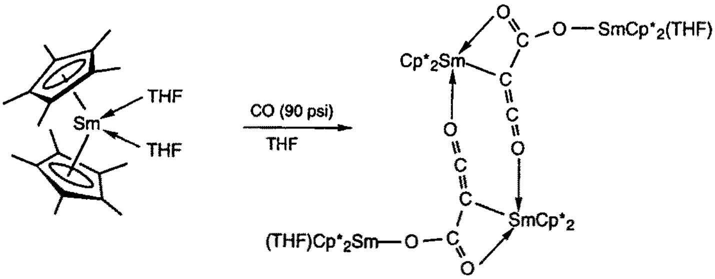
(42)

The pyridyl complex Cp$^*_2$Y(2-pyridyl) reacts both with excess (1 bar) and 1 equivalent of CO to yield a μ-η^2:η^2-dipyridylketone fragment by unexpected CO insertion (Eq. 43) [283]. The Y–O bond distances are in the range of bridging alkoxide ligands (Table 18).



(43)

The samarium(II) reagent Cp$^*_2$ Sm(THF)$_2$ affords a reductive homologenation of CO to a ketene carboxylate (Eq. 44 [284]. The reaction sequence formally involves two one-electron reductions, CO coupling and a remarkable cleavage of a CO bond. The O_2CCCO unit forms one Sm-O-σ-bond (Table 18).

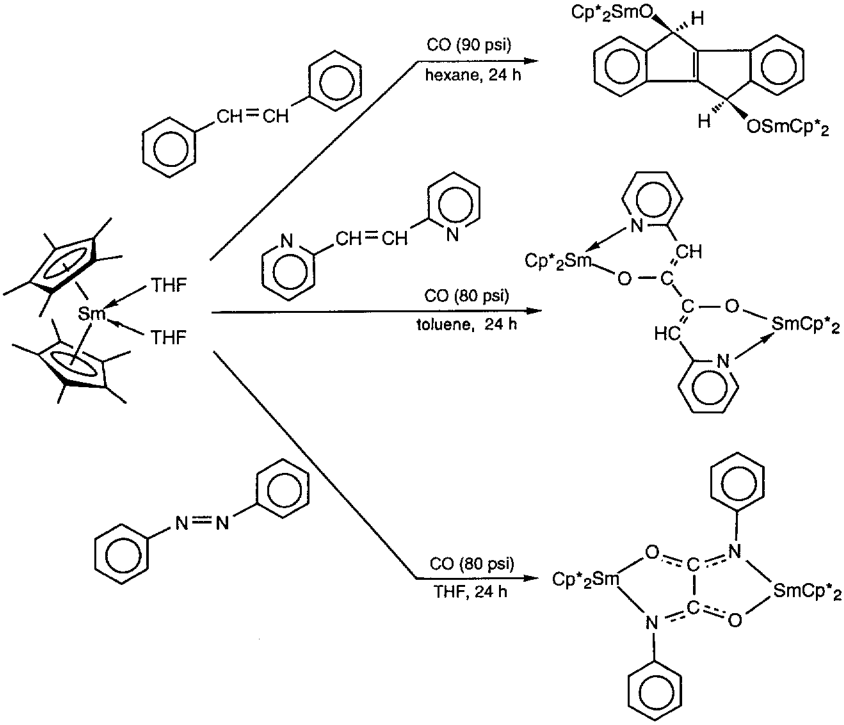


(44)

This unique reactivity was subsequently utilized in the functionalization of unsaturated hydrocarbon substrates with CO (Scheme 39) [285, 286]. In the course of these studies the stereospecific synthesis of a diolato unit was observed via a samarium-mediated CO and CH (alkene) activation. A bridging trans-5,10-dihydroindeno[2,1-*a*]-5,10-diolate ligand forms terminal Sm-O bonds in [Cp$^*_2$Sm]$_2$($O_2C_{16}H_{10}$) and its THF adduct. Two molecules of CO are formally inserted into the carbon carbon double bond of 1,2-di-2-pyridylethene to form a terminal bisenolate moiety [286] (Table 18).

Samarium-mediated functionalization also occurs in the case of N=N bonds [287]. A high yield (80%) double insertion of carbon monoxide into the N=N bond of the dianion of azobenzene was observed to formally yield a *N,N'*-diphenyloxamide. Insertion was not observed in the case of the Ph_2N_2- monoanion. The Sm-O distances are between the values typical for terminal Ln(III)-OR σ-bonds and Ln ← OR_2 donor bond lengths (Table 18).

The enantioselective formation of C-C bonds by addition of carbonyl compounds to lanthanide alkoxides was emphasized in the foregoing section. Also, in situ formation of lanthanide enolate species from organolanthanides, e.g., of type X_2LnR, and the importance of chelating/nonchelating in aldol condensations were pointed out. C-C bond forming and breaking reactions were modelled by use of the well-defined organolanthanide complexes $Cp^{\ddagger}_2 Ln[CH(SiMe_3)_2]$ [248].

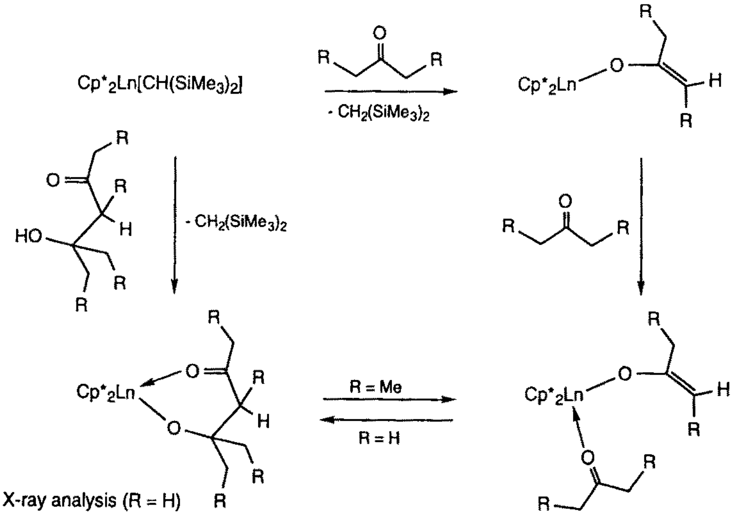


Scheme 39. Functionalization of double bonds by CO

It was found that the reactivity towards ketones is dominated by hydrogen transfer reactions (C-H bond activation/deprotonation) resembling chemistry of the main group elements Li, Na, B, Al. Organolanthanide based intermediates as ketone adducts, enolates and aldolates could be isolated according to Scheme 40. C-C coupling was obtained in the acetone reaction. The "acetone-aldolate" was also accessible by reaction of $Cp^{\ddagger}_2 Ln[CH(SiMe_3)_2]$ with β-hydroxyketone. The molecular structure of $Cp^{\ddagger}_2 Ce[OCMe_2CH_2C(=O)Me]$ contains a formally

8-coordinate cerium whose two oxygen (aldolate) contacts differ significantly (Table 18). Five atoms of the resulting 6-membered ring are coplanar within 0.07 Å with one C-atom 0.69 Å out of the plane and reveal a bite angle of 73.7(1)°. The same reaction with the sterically more crowded β-hydroxyketone ($R = Et$) results in C-C bond cleavage and formation of an enolate/ketone adduct complex and suggests that the differences in reactivity are thermodynamic in origin.

A real active butadiene polymerization catalyst could be isolated from the ternary system "$Nd(O\mathit{i}Pr)_3$-$AlEt_3$-$AlEt_2Cl$" [288]. Single crystals were grown from a toluene/hexane solution over a period of several months and found to polymerize effectively butadiene to high *cis*-1,4 polymers. The molecular structure revealed a fascinating polynuclear heterobimetallic complex which can best be described by the formula $[Al_3Nd_6(\mu_3\text{-}Cl)_6(\mu_2\text{-}Cl)_6(\mu_2\text{-}Et)_9Et_5(O\mathit{i}Pr)]_2$.



Scheme 40. Metal-templated synthesis of an "acetone-aldolate" ligand

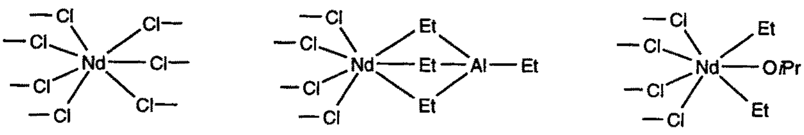


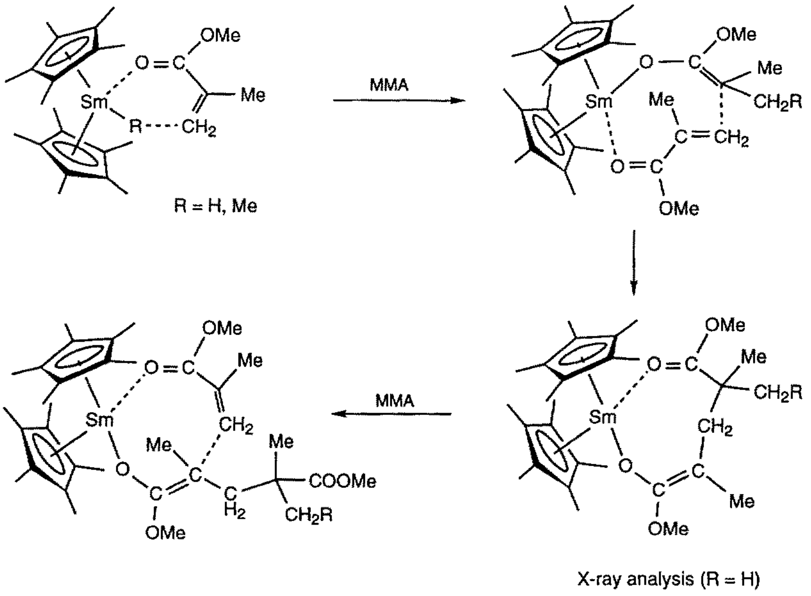
Fig. 37. Coordination environments found in $[Al_3Nd_6(\mu_3\text{-}Cl)_6(\mu_2\text{-}Cl)_6(\mu_2\text{-}Et)_9Et_5(O\mathit{i}Pr)]_2$ [288]

The neodymium atoms are placed in three different environments as depicted in Fig. 37. However, all neodymium atoms are 7-coordinate adopting a distorted mono capped prismatic geometry. Most interesting structural feature are the presence of terminal ethyl and isopropoxide ligands at neodymium. More simple molecular arrangments were found in ligand related complexes $Ln[(\mu$-

O*t*Bu)AlMe$_2$(μ-Me)]$_3$ (Ln = La, Pr, Nd, Y), Y[(μ-O*t*Bu)AlMe$_2$(μ-Me)]$_2$(O*t*Bu)(THF) and (O*t*Bu)(Cl)(THF)$_2$Y[(μ-O*t*Bu)AlMe$_2$] (Sect. 6.1) [225].

Another real active species was isolated form the reaction of [Cp*$_2$SmH]$_2$ with two equivalents of MMA monomer (methyl methacrylate) [289]. Organolanthanide complexes of type "Cp$_2$LnR" (R = H, alkyl) are not only effective precatalysts in the polymerization of nonpolar monomers such as ethylene, but also initiate the ideal living polymerization of MMA [289–291].

High molecular weight polymers ($M_n > 100 \times 10^3$) with extremely low polydispersity ($M_w/M_n = 1.02$) were found. In addition highly syndiotactic polymerization (95.3%) occurred at low temperature (– 95 °C). The molecular structure of the active catalyst exhibits two oligomerized MMA units which chelate the metal center via Sm-O interactions (Scheme 41). A terminal Sm-O(enolate) bond and an elongated Sm-O contact result in an 8-membered ring structure achieving a bite angle of 94.0(3)° (Table 18). Meanwhile, stereocontrolled polymerization of MMA could be achieved by using C$_1$-symmetric organolanthanides [291].



Scheme 41. Proposed initiation mechanism for syndiotactic polymerization of MMA

6.3 Precursors to Ceramic Materials

Lanthanide alkoxides are used as promising precursors to electronic and ceramic materials. As a consequence, slogans such as "volatility" and "high solubility" are often found in the recently published data. The attribute "solubility" is easier accomplished and hence reflected in numerous investigations in sol gel processes [292, 293]. Usually, lanthanide alkoxides display a high reactivity towards water and the formation of hydroxides or oxides with liberation of volatile alcohol is extremely facile. Chemical additives such as β-diketonates or donor-functionalized alcohols are used in order to control solubility and hydrolysis rates [98, 123, 294, 295]. Under these conditions already less soluble small lanthanide alkoxide clusters derived from O*i*Pr and O*t*Bu qualify for this technology. The additive enhances the solubility of the alkoxide precursor by facile ligand exchange reactions and impedes hydrolysis due to chelation [4]. Thus more appropriate rheological conditions (stabilization of homogenous gels, "network former") are obtained.

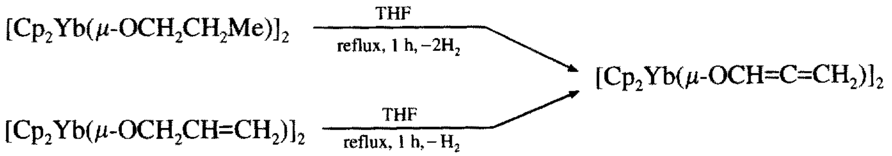
Applications of lanthanide alkoxides based on volatility such as in MOCVD processes are very limited [3, 296]. β-Diketonates are still easier to handle, particularly because of their stability against moisture [297–299]. However, as the high stability of β-diketonates excludes their use as single component precursor in sol gel technology, decomposition of Ln(III)-β-diketonates to oxide ceramics as a rule requires the presence of an oxygen source like a reactive gas (THF, N_2O, O_2) or an O_2-plasma in plasma enhanced chemical vapor deposition [300, 301]. In contrast, CeO_2 can be obtained from the β-diketonate precursor without a reactive gas [302]. The use of an additional reactive component might be avoided in alkoxide-based processes. Early pyrolysis experiments on zirconium and yttrium alkoxides support this theory [303, 304]. More recently, alkoxide complexes of early transition metals such as Ti, Zr, Ta, Mo, W displayed "single-source-precursor" character in the formation of metal oxides by thermal and photolytic degradation [305–307]. Thermally induced ligand degradation was proven by X-ray crystallography in the $Ln(tritox)_3$-$Ln(ditox)_3$ conversion (see below) [29] and in the dehydrogenation of organolanthanide alkoxides according to Scheme 42 [308].

Thermal decomposition of homo- and heterodinuclear Schiff base complexes to crystallographically pure species of Ln_2O_3 and $Ln^1Ln^2O_3$ was reported (Scheme 43) [309].

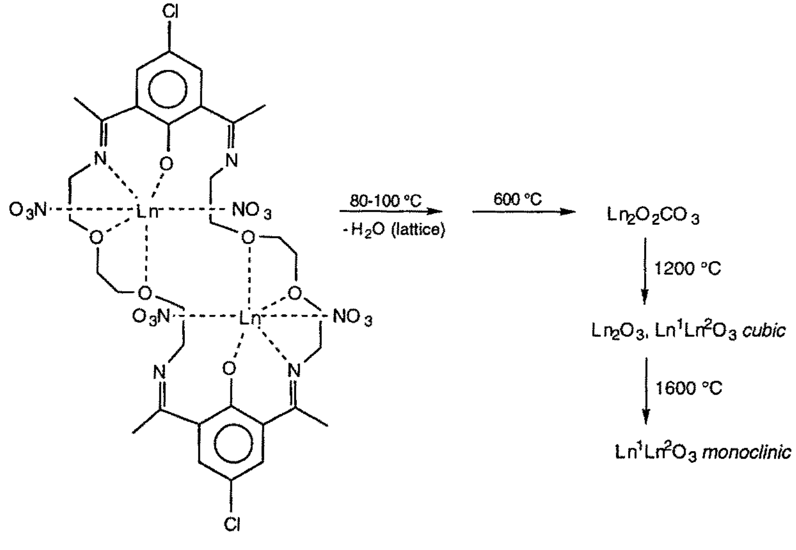
The oxidic species show a similar magnetic moment as the complex precursor (μ_B: $DyNdL(NO_3)_4 \cdot 2H_2O$, 8.17; $DyNdO_3$, 8.23) [309]. Secondary ion mass spectrometry (SIMS) was successfully applied to analyze involatile inorganic species such as Ln^+, LnO^+, $LnOH^+$ and $Ln(OH)_2^+$ [310]. Fast atom bombardment mass spectrometry (FABS) even allowed the observation of novel gaseous polyatomic binary and ternary oxides such as $Ln_9O_{13}^+$ and $YTm_5O_9^+$ [311].

Thermal decomposition of mixed lanthanide copper complexes derived from such compartmental ligands (Fig. 38) resulted in the formation of $CuLnO_4$ + CuO according to X-ray powder diffraction analysis and electron microscopy investigations [174b]. Thermogravimetric analysis of lanthanide copper complexes with a mixed oxygen-based ligand sphere including aminofunctionalized alcohols were also investigated and formation of oxidic material concluded [139–141]

Typical source temperatures of $Y(thd)_3$ in MOCVD of HTS-YBCO are in the range of 100–160 °C [299]. Meanwhile alkoxide complexes of similar volatility are available. Tables 19 and 20 show the sublimation behavior of lanthanide alkoxides in order of their classification. Of course, "subjective" detection of sublimation conditions and thermal gravimetric analysis allow only a first screening of the alkoxide precursor. They cannot replace the more meaningful



Scheme 42. Thermally induced dehydrogenation



Scheme 43. Thermal degradation of Schiff base complexes

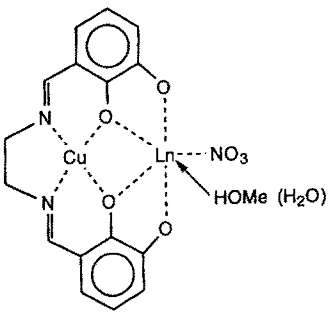
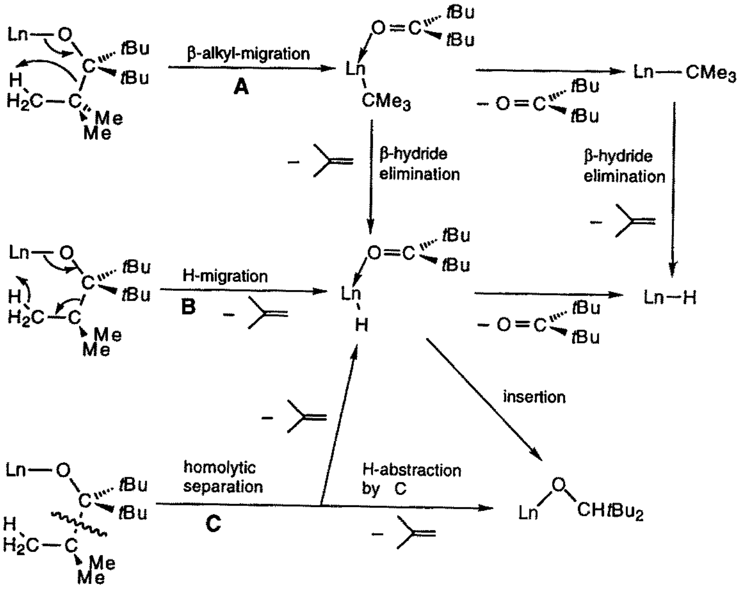


Fig. 38. Heterobimetallic Schiff base complexes potential precursors to oxidic ceramics

vapor pressure measurements [312]. Nevertheless, CHF-alkoxides and CHdo-alkoxides are apparently the most encouraging systems. A drawback with CHF-alkoxides is their tendency to incorporate fluoride upon thermal degradation [76b].

6.3.1 CH-Alkoxides

The sterically most congested CH-alkoxides Ln(tritox)$_3$ is thermally labile and decomposes to Ln(ditox)$_3$ by loss of isobutene [29, 38]. In addition, a small quantity of di-*tert*-butylketone indicates the formation of a Ce(III) hydride species. Ln(ditox)$_3$ can be obtained in analytically pure form via sublimation. Scheme 44 describes the mechanistic scenario which was suggested for the Ce(tritox)$_3$ system [29].



Scheme 44. Mechanistic scenario suggested for the thermal degradation of Ce(tritox)$_3$ [29]

Experimental results favor the homolytic cleavage of the C-C bond according step C. *t*Bu radicals could be trapped as HOC*t*BuPh$_2$ from the Ce(tritox)$_3$/OCPh$_2$ system. The determination of the approximate thermolysis half-time ($t_{1/2}$: H-tritox > Ce(tritox)$_3$ > Li(tritox)$_3$ $\gg$ Li(12-crown-4)tritox) is consistent with the increasing charge separation between M and O from M = H to M = Li(12-crown-4). Increased negative charge on the oxygen atom should facilitate C-C bond homolysis according to step **C**. However, the thermal behavior is inconsistent with steps **A** and **B** since intramolecular approach as

Table 19. Sublimation behavior of selected lanthanide CH-alkoxides

Compound	Sublimation Temp. [°C]	Pressure [torr]	Ref.
$Yb_5O(OiPr)_{13}$	220	10^{-2}	[9b]
"$La(OtBu)_3$"	280	10^{-4}	[17b]
$La_3(OtBu)_9(HOtBu)_2$	240	10^{-3}	[10]
$Y_3(OtBu)_9(HOtBu)_2$	235	10^{-2}	[10]
$Y_3(OtAm)_9(HOtAm)_2$	150	10^{-3}	[10]
$\{La(OCMe_2iPr)_3\}$	135^a	10^{-3}	[10]
$\{Yb(OCMe_2iPr)_3\}$	170^a	10^{-3}	[10]
$\{La(OCMeEtiPr)_3\}$	150^a	10^{-3}	[10]
$\{Y(OCEt_3)_3\}$	225^a	10^{-2}	[10]
$[Nd(OCHtBu_2)_3]_2$	175	10^{-3}	[38]
$[Dy(OCHtBu_2)_3]_2$	240	10^{-3}	[38]
$[Tm(OCHtBu_2)_3]_2$	> 220	10^{-3}	[40]
$\{Y(OCiPr_3)_3\}$	200^a	10^{-3}	[35]
$\{Nd(OCiPr_3)_3\}$	220^a	10^{-3}	[35]
$Y(OCiPrtBu_2)_3$	160	10^{-3}	[39]
$Nd(OCtBu_3)_3$	150 (dec.)	10^{-3}	[38]
$Nd(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_3$	> 240	10^{-3}	[16]

^{a} Dinuclear species detected in mass spectra

Table 20. Sublimation behavior of selected lanthanide CHF- and CHdo-alkoxides

Compound	Sublimation Temp. [°C]	Pressure [torr]	Ref.
$Ln[OCH(CF_3)_2]_3 \cdot 2NH_3$	120–140 (dest.)	0.08	[76b]
$Y[OCMe(CF_3)_2]_2 \cdot xEt_2O$	75–100^{a,b}	10^{-2}	[78]
$\{La[OCMe(CF_3)_2]_3\}_n$	130 (dec)	10^{-2}	[80a]
$Eu[OCMe(CF_3)_2]_3(diglyme)$	110–140	10^{-2}	[80b]
$Lu_4(O)(OH)(OCMe_2CH_2OMe)_9$	> 220	10^{-3}	[106]
$[Lu(OCMe_2CH_2OMe)_3]_2$	95	10^{-3}	[106]
$\{Nd(OCHtBuCH_2OEt)_3\}$	175	10^{-3}	[120]
$\{Nd(OCHtBuCH_2NEt_2)_3\}$	150	10^{-3}	[120]
$Nd(OCtBu_2CH_2OEt)_3$	125	10^{-3}	[120]
$Nd(OCiPr_2CH_2OEt)_3$	115	10^{-3}	[120]
$Y(OCiPr_2CH_2OEt)_3$	95	10^{-3}	[120]
$Y[OSitBu_2(CH_2)_3NMe_2]_3$	115	5×10^{-4}	[118]
$Ce[OSitBu_2(CH_2)_3NMe_2]_3$	135	5×10^{-4}	[118]
$Y[OSitBu_2(CH_2)_3NMe_2]_3[OSitBu_2(CH_2)_3NMe_2H]$	125	5×10^{-4}	[118]

$^a x = \approx 0.3$

^{b} Dinuclear species detected in mass spectra

a prerequisite for β-alkyl-(**A**) and H-(**B**) migration should be hampered by $M \cdots OCtBu_3$ distancing [33]. For similar steric reasons, a decrease in the size of the lanthanide center should discourage intramolecular approach of the ligand and hence decomposition according to steps **A** and **B**.

However, with the significantly smaller thulium formation of the ditox derivative is observed upon attempted sublimation [40]. In addition, use of the slightly less bulky proditox ligand affords a thermally stable and sublimable $Y(proditox)_3$ [39]. Obviously the thermal lability of the $Ln(tritox)_3$ is caused by

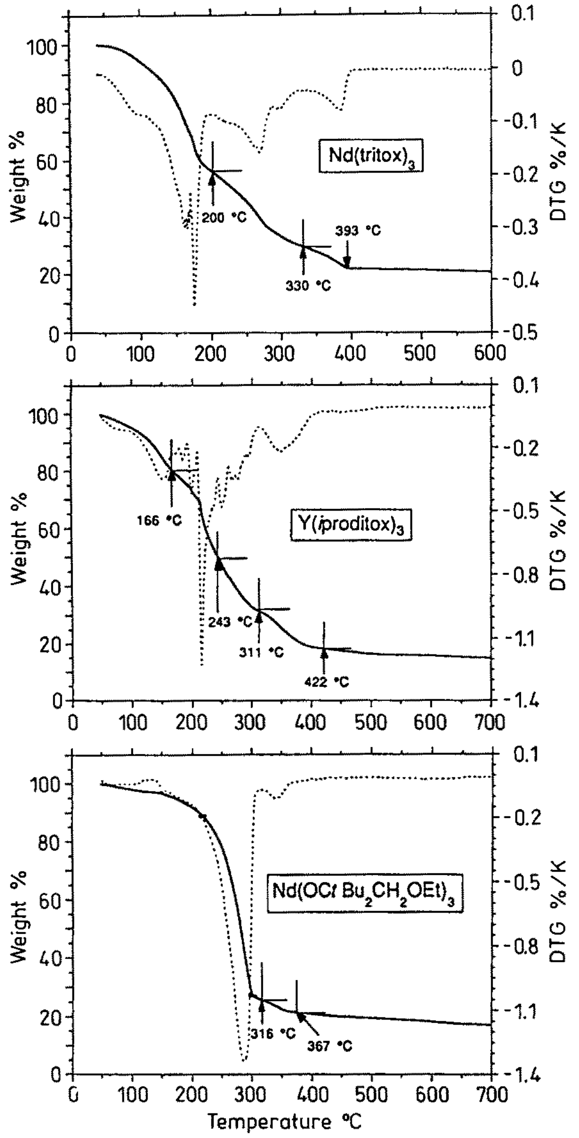


Fig. 39. Thermogravimetric analysis of lanthanide alkoxides (programed heating rate 5 K min^{-1}), observed in an atmosphere of predried helium gas at a measured flow rate of 45 ml min^{-1}) [16]

the thermal instability of the tritox ligand [54, 313]. The sublimation behavior of homoleptic complexes derived from CH-alcohols of reduced bulk as triisopropylmethanol points to dimeric species in the solid state [35].

In contrast, the Ln(silox)$_3$ system appears to be thermally rather inert and the neodymium derivative sublimes at around 340 °C with slight decomposition [16]. The strength of the Si-O bond and the unfavorable separation of silyl cations (route C) might explain this behavior [34]. Thermal stability of the silox ligand was also detected in Ba$_2$(silox)$_4$(THF) [314].

Thermogravimetric examination of Nd(tritox)$_3$ (Fig. 39), Nd(ditox)$_3$ and Y(proditox)$_3$ (Fig. 39) shows decomposition in several consecutive steps [16, 38]. The observed mass fragments can be assigned to typical ligand fragments (tritox, ditox: $m/z = 57, 87$; proditox: $m/z = 57, 112$). The thermogram of Nd(tritox)$_3$ also revealed the formation of tBu$_2$CO ($m/z = 142$).

6.3.2 CHF-Alkoxides

Solvent-free CHF-alkoxides show decomposition upon attempted sublimation [78–80]. However, mononuclear adduct complexes show remarkable volatility (Table 20). While neutral co-ligands such as THF, NH$_3$, Et$_2$O or HOtBu partly separate off during sublimation in the temperature range 90–150 °C, chelating co-ligands afford complete sublimation, as shown with Ln(hftb)$_3$(diglyme) [78].

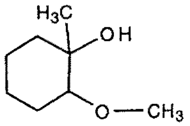


Fig. 40. Donor-functionalized *cyclo*-hexanols – rigid CHdo-alcohols

Such multiply chelating co-ligands were previously applied to the successful generation of volatile complexes of the alkaline earth metals [315]. Thermogravimetric analysis of Ln[OCH(CHF$_3$)]$_3\cdot$2NH$_3$ (Ln = Y, Yb), conducted in helium atmosphere, show a gradual weight loss with increasing temperature up to 250 °C. The thermogram of the lanthanum compound shows three consecutive steps [76b].

6.3.3 CHdo-Alkoxides

Due to their excellent sublimation behavior CHdo-alkoxides are promising candidates for OMCVD processes [316]. Similarly composed siloxide complexes also possess remarkable volatility [118]. However, the strong Si-O bond might favor incorporation of silicon into the deposited material. Thermogravimetric analysis study on Nd(OCtBu$_2$CH$_2$OEt)$_3$ displays a sharp main decomposition step (Fig. 39) [16]. Ligand fragmentation could be detected in the coupled mass spectrometer. This decomposition characteristic is typically observed for very volatile species as shown for Ln(RCp)$_3$ [16], Ln[N(SiMe$_3$)$_2$]$_3$ [16, 317] and Ln(β-diketonates)$_3$ [318].

CHdo-alcohols containing a rigid, saturated hydrocarbon ring (Fig. 40) produce complexes of lower volatility ($> 230\,°C/10^{-3}$ torr) comparable to that of homoleptic monomeric aryloxides [16, 57].

7 Conclusion and Perspective

Simple CH-alkoxides continue to reveal surprising new structure chemistry and the composition of $Ln(OMe)_3$ and $Ln(OEt)_3$ is not yet determined. Mononuclear lanthanide aryloxide complexes are well-examined and are the only fully characterized 3-coordinate, homoleptic $Ln(OR)_3$ species. The variation of the steric environment in pure CH- and CHF-alkoxides with respect to volatility (molecular mass optimization) seems to be rather exhausted. It was shown that functionalization can ensure volatility and although the entire MOCVD-business gets somewhat stuck, CHF- and CHdo-alkoxides are promising alternatives to the β-diketonates. Sol gel technology can fall back on highly soluble CH- and CHdo-alkoxides.

However, fine-tuning of CHdo-alkoxides, not only with regard to volatility, has just started and offers much more scope. In particular, tailor-made CHdo-alkoxides may provide a new option for the topic "lanthanide alkoxides in selective organic synthesis". Unique and high selectivities of organic transformations mediated by organolanthanides are often explained in terms of strong oxophilicity, the hard and soft acid and base (HSAB) theory and chelating effects. Right now a broad industrial application of organolanthanides is hampered by their sensitivity to moisture. However, CHdo-alkoxides can be extraordinarily stable even to moisture as has been impressively shown by use of BINOL and calixaren ligands. The role of a spectator ligand in heteroleptic organometallic compounds could also be ascribed to this ligand type. In addition, CHdo-alcohols can ensure well-defined and low agglomerated catalysts which are desired in homogenous catalytic reactions and therefore research will focus on functionalized, chelating alkoxide systems. Derivatives of Ce(IV) and Ln(II), and particularly Sm(II), should be included in the concept of this new epoch of alkoxide complexes since their application in organic synthesis has a long history. The ultimate goal of a "single-component-catalyst" which combines donor-functionality, solubility, stability against moisture, and heterometal incorporation seems to be possible. Molecular modelling will prove to be a valuable and convenient tool for ligand design.

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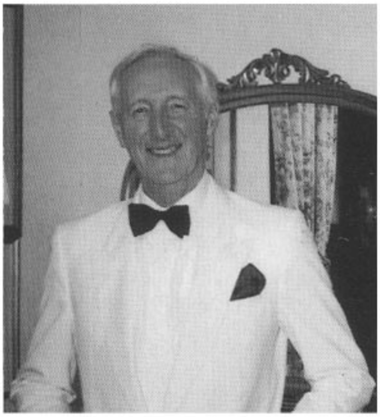
Reiner Anwander

Appendix – A Personal Sketch



I would like to dedicate this article to Donald C. Bradley, who initiated and made significant contributions to the area of lanthanide alkoxide chemistry. I had the pleasure of meeting him several times in stimulating discussion sessions. Professor Donald Bradley was born on 7 November 1924. He received his university education at Birkbeck College (University of London, UK) where he obtained the B.Sc. (1st Class Honors in Chemistry, 1946), Ph.D. (Physical Inorganic Chemistry, 1950) and D.Sc. (1959) degrees.

His academic career started at Birkbeck College where he was Lecturer in Inorganic Chemistry from 1949 to 1959. His first professorial appointment was at the University of Western Ontario, Canada, from 1959 to 1965. In 1965 he was appointed to the Chair of Inorganic Chemistry at Queen Mary College, London, UK, and served as Head of Department from 1979 to 1983. Since 1965 he has served on many committees at Queen Mary College and the University of London and has also played an active role in the Royal Society of Chemistry. In 1987 Professor Bradley was made Emeritus Professor of Inorganic Chemistry of the University of London and became a Fellow of Queen Mary College in 1988.

During the past 40 years he has conducted pioneering research in the synthesis of novel metallo-organic compounds such as metal alkoxides and oxoalkoxides, metal dialkylamides, metal dithiocarbamates, metal organo-imido complexes and bis-trimethylsilylamides of the transition metals and lanthanides. In particular, his research on (lanthanide) alkoxide chemistry helped to unravel the interrelation between ligand bulk, molecular weight and the volatility of molecular complexes. For example, by introducing fluorinated tertiary alkoxide ligands he lent the lanthanide metals "wings". Another highlight appeared as a consequence of this work, namely the establishment of the very lowest coordination numbers for transition metals and lanthanides. The monomeric bis-trimethylsilylamides of the lanthanides are now key precursors in synthetic chemistry. His work clearly documents "the importance of carrying out purely academic research for its own sake". The metal alkoxides synthesized originally as "academic curiosities" are "now helping new industrial processes to take off". Recently his research has involved the synthesis of volatile organometallic compounds of aluminium, gallium and indium–more "metals with wings" for the deposition of III-V semiconductors by chemical vapor deposition.

Professor Bradley has published over 250 original papers. In recognition of his work he was elected to the Fellowship of the Royal Society (1980) and awarded the Ludwig Mond Medal and Lectureship of the Royal Society of Chemistry (1987).

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Lanthanide Metallocenes in Homogeneous Catalysis

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Dedicated to Prof. Walter Schwartr on the occasion of his 65th birthday

Table of Contents

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This comprehensive review summarizes recent developments and trends in the use of lanthanide metallocenes in homogeneous catalysis. σ-Alkyl and hydride complexes such as $(C_5Me_5)_2LnCH(SiMe_3)_2$ and $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ play a key role as precatalysts in organolanthanide mediated reactions. The design and synthesis of such complexes is outlined first. This is followed by a description of various processes catalyzed by lanthanide metallocenes such as olefin, diene, and alkyne transformations. Olefin transformations include oligomerizations and polymerization as well as a variety of addition reactions. In some instances catalyst activities are exceedingly high as compared to conventional *d*-transition metal catalysts.

1 Introduction

The year 1954 marks the beginning of organolanthanide chemistry, when Birmingham and Wilkinson described the tris(cyclopentadienyl)lanthanide complexes, $Ln(C_5H_5)_3$ [1]. However, rapid development of this new area of organometallic chemistry was hampered by the intrinsic instability of organolanthanide compounds towards moisture and oxygen. The highly oxophilic character of the 4f-elements requires rigorous exclusion of traces of air and moisture during preparation and characterization of organometallic compounds of these metals. With today's more sophisticated experimental and analytical techniques organolanthanides and –actinides are routinely synthesized and handled and their unique properties are easily studied. Historically, the early discovery of $Ln(C_5H_5)_3$ was followed by a period of relative stagnation which lasted about two decades. The past twenty years, however, have witnessed an enormous and exciting development of organolanthanide chemistry [2–7]. This spectacular growth in research activities is mainly due to the fact, that many organo-*f*-element complexes exhibit unique structural and physical properties and many of them are highly active in various catalytic processes. In fact, the catalytic activity of certain organolanthanide hydrocarbyls and hydrides is often dramatically higher than that of comparable d-transition metal catalysts.

Chemists became first interested in catalytic applications of organolanthanides when it turned out, that some lanthanide organometallics are highly active as olefin polymerization catalysts [8]. The first indications of catalytic activity of organolanthanides came from the observation, that active species were formed when lanthanide oxides, halides, or alkoxides were treated with co-catalysts such as lithium alkyls, aluminium alkyls, or other hydrocarbyl transfer reagents. The transient lanthanide σ-hydrocarbyl lanthanide species were found to catalyze the cracking of hydrocarbons as well as oligomerizations and polymerizations of olefins [7, 8]. Later, when well-defined organolanthanide complexes became available, it was found that some of them are also effective polymerization catalysts. For example, polymerization of ethylene or butadiene was observed in the presence of bis(cyclopentadienyl)lanthanide hydrocarbyls [7], (cyclooctatetraenyl)cerium complexes [8], as well as lanthanide allyl complexes [8]. Butadiene polymerization was most effectively catalyzed by anionic tetra(allyl)lanthanide complexes.

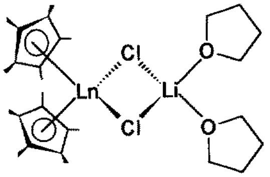
A review article covering the use of organolanthanides in homogeneous catalysis has been published by Watson and Parshall in 1985 [9]. Other review articles on special aspects of organolanthanide catalysis (e.g. C–H activation) have also been published [10–12]. Most catalytic applications of organolanthanide complexes involve transformations of olefins or dienes and, to a lesser extent, alkynes. Recent research in this area has focussed on extending the scope of catalytic reactions involving organolanthanides and on varying the bis(cyclopentadienyl) ligand coordination sphere in order to achieve new catalytic applications. Especially variations of the cyclopentadienyl substituents or the use of ring-bridged cyclopentadienyl ligands has led to novel catalytic applications such as oligomerization and isospecific polymerization of α-olefins, hydrocyclization of α,ω-dienes, C–C σ-bond activation, and hydroamination/cyclization of olefins.

2 Catalyst Preparation

Probably the most useful and active catalytic species in various reactions are lanthanide metallocenes of the type $(C_5Me_5)_2LnR$ (R = $CH(SiMe_3)_2$ or H; Ln = Y, La, Ce, Nd, Sm, Lu) [6, 7]. They may act as homogeneous catalysts or precatalysts. The hydrocarbyls $(C_5Me_5)_2LnR$ (R = Me,$CH(SiMe_3)_2$) are generally made by alkylation of readily available halide precursors. Synthesis and characterization of "ate" complexes of the type $(C_5Me_5)_2Ln(\mu\text{-}X)_2ML_2$ (X = Cl, Br, I; M = Li, Na, K; L = THF, Et_2O,1/2DME) have been described in detail in a number of publications. These complexes are the most common type of $(C_5Me_5)_2Ln$ derivatives. They are generally the initial products when anhydrous lanthanide trihalides are reacted with two equivalents of alkali metal pentamethylcyclopentadienides [6, 7, 13, 14]. The first compound of this type to appear in the literature was $(C_5Me_5)_2Nd(\mu\text{-}Cl)_2Li(THF)_2$, made by reacting $NdCl_3$ with $Li(C_5Me_5)$ in THF solution [15]. A typical reaction sequence is given in

Eq. (1).

$$LnCl_3 + 2\ Li(C_5Me_5) \xrightarrow{THF} (C_5Me_5)_2\,Ln(\mu\text{-}Cl)_2Li\,(THF)_2 + LiCl \quad (1)$$



The vast majority of these reactions have been carried out with the lanthanide *trichlorides*. $Li(C_5Me_5)$, $Na(C_5Me_5)$, and $K(C_5Me_5)$ have been used as pentamethylcyclopentadienyl transfer reagents, and suitable co-ligands are diethyl ether, THF, and DME or TMEDA. In most cases the resulting "ate" complexes are well-crystallizing solids which are surprisingly soluble in organic solvents despite the presence of coordinated alkali metal halide. Complexes of this type have been synthesized for all lanthanide elements except promethium [6,7]. As often, the cerium derivatives are the most air-sensitive members of the series. In the presence of traces of air, the bright yellow cerium complexes instantaneously turn purple or brown. However, it has so far not been possible to isolate a well-defined cerium(IV) species from these oxidized materials. On the other hand, treatment of inorganic cerium(IV) precursors with $Li(C_5Me_5)$ invariably produced $(C_5Me_5)_2Ce(\mu\text{-}Cl)_2LiL_2$ ($L = Et_2O$, pyridine) species containing trivalent cerium [16]. The compounds have been characterized by various spectroscopic methods as well as X-ray crystal structure analyses [14, 17]. Other structurally characterized complexes of this type are $[(C_5Me_5)_2Ce(\mu\text{-}Cl)_2K(THF)]_n$, [18] $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Na(DME)_2$, [13] and $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(Et_2O)_2$ [6, 7]. As a typical example the molecular structure of $(C_5Me_5)_2Ce(\mu\text{-}Cl)_2Li(Et_2O)_2$ [14] is shown in Fig. 1.

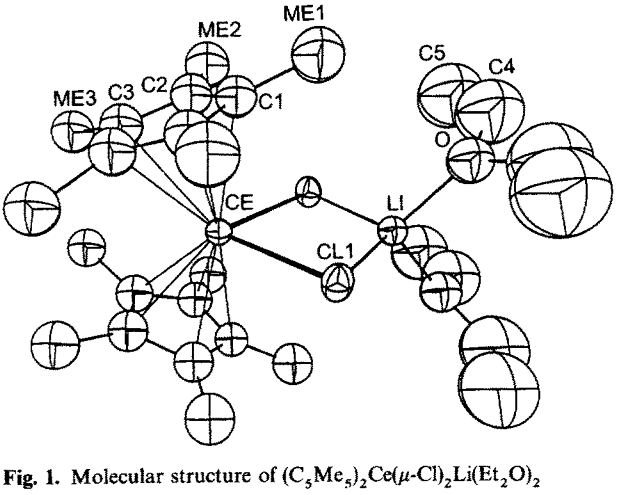
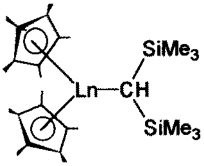


Fig. 1. Molecular structure of $(C_5Me_5)_2Ce(\mu\text{-}Cl)_2Li(Et_2O)_2$

Of great importance as precatalysts in organolanthanide-catalyzed processes are lanthanide hydrocarbyls containing the bulky bis(trimethylsilyl)methyl ligand. They are also the most suitable precursors for the preparation of the dimeric hydrides $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$. Such compounds can be isolated completely free of coordinating solvents and alkali metal halides Eq. (2) [19–25].

$$(C_5Me_5)_2Ln(\mu\text{-}Cl)_2Li(Et_2O)_2 + LiCH(SiMe_3)_2 \longrightarrow (C_5Me_5)_2LnCH(SiMe_3)_2 + 2\,LiCl + 2\,Et_2O \qquad (2)$$

Ln = Y, La, Ce, Nd, Sm, Lu



In the case of yttrium, salt-free $(C_5Me_5)_2YCl(THF)$ is the preferred starting material [20]. The molecular structure of $(C_5Me_5)_2YCH(SiMe_3)_2$ has been determined, showing α-C–H–Y and γ-Me···Y agostic interactions. Both types of secondary interactions relieve the electronic unsaturation in the formally 14-electron complex [20]. A somewhat different behavior was reported for the corresponding organocerium hydrocarbyl $(C_5Me_5)_2CeCH(SiMe_3)_2$ [21,26]. The original preparation called for treatment of the "ate" complex $(C_5Me_5)_2Ce(\mu\text{-}Cl)_2Li(THF)_2$ with $LiCH(SiMe_3)_2$. However, the yields were low because the LiCl by-product (two equivalents) reacts with $(C_5Me_5)_2CeCH(SiMe_3)_2$. A more reliable preparation of $(C_5Me_5)_2CeCH(SiMe_3)_2$ involves the reaction of $[(C_5Me_5)_2CeCl]_n$ with the organolithium reagent, Eq. (3):

$$[(C_5Me_5)_2CeCl]_n + LiCH(SiMe_3)_2 \longrightarrow (C_5Me_5)_2CeCH(SiMe_3)_2 + LiCl \qquad (3)$$

The molecular structures of both $(C_5Me_5)_2CeCH(SiMe_3)_2$ and $(C_5Me_5)_2NdCH(SiMe_3)_2$ [23] (Fig. 2) have been determined by X-ray diffraction. Both complexes exhibit an agostic α-C–H–Ln interaction as well as a secondary β-Si–Me–Ln interaction.

In several recent studies on organoyttrium-catalyzed reactions the σ-methyl complex $(C_5Me_5)_2YMe(THF)$ has been employed as a highly active precatalyst (cf. Sect 4.1, 4.2. and 5.3). The main advantage of this material is that it is much more readily available than the corresponding bis(trimethylsilyl)methyl derivative. $(C_5Me_5)_2YMe(THF)$ can be synthesized in one pot by the reaction of anhydrous YCl_3 with two equivalents of $Li(C_5Me_5)$ followed by addition of MeLi [27].

Organolanthanide hydrides of the type $(C_5Me_5)_2LnH$ are also of great importance as rare earth-based homogeneous catalysts. Thus this group of compounds has been thoroughly investigated and elaborate methods for their synthesis have been designed [19–21, 28–31]. Since a $(C_5Me_5)_2LnH$ fragment is

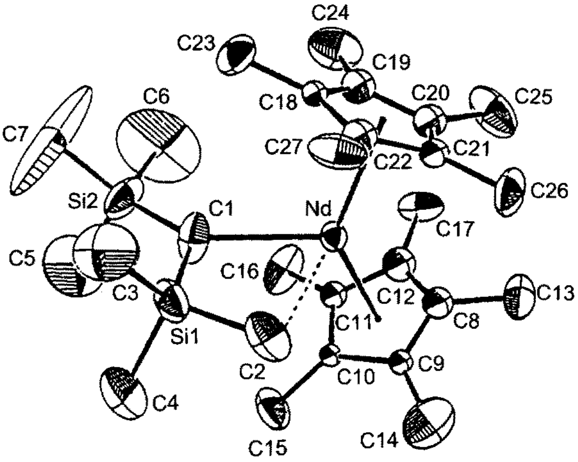


Fig. 2. Molecular structure of $(C_5Me_5)_2NdCH(SiMe_3)_2$

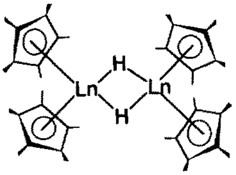
coordinatively unsaturated, these hydride species are usually isolated as dimers or solvated species. Bis(pentamethylcyclopentadienyl)lanthanide hydrides are generally prepared by hydrogenolysis of the corresponding hydrocarbyls. Unsolvated hydrocarbyls containing the bulky $CH(SiMe_3)_2$ ligand have been shown to be especially useful for the preparation of hydrides. A typical synthesis starting from the THF adduct of yttrium trichloride is outlined below, Eqs. (4)–(6) [32].

$$YCl_3(THF)_3 + 2Na(C_5Me_5) \xrightarrow{THF} (C_5Me_5)_2YCl(THF) + NaCl \quad (4)$$

$$(C_5Me_5)_2YCl(THF) + LiCH(SiMe_3)_2 \xrightarrow{Et_2O} (C_5Me_5)_2YCH(SiMe_3)_2 + LiCl + THF \quad (5)$$

$$2(C_5Me_5)_2YCH(SiMe_3)_2 + H_2 \longrightarrow [(C_5Me_5)_2Y(\mu\text{-}H)]_2 + 2CH_2(SiMe_3)_2 \quad (6)$$

The dimeric cerium, neodymium, and samarium hydrides $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ (Ln = Ce, Nd, Sm) have been prepared analogously by hydrogenation of $(C_5Me_5)_2LnCH(SiMe_3)_2$ [19,23,33].



Two factors are important for the success of this preparation: Due to the high steric demand of the $CH(SiMe_3)_2$ ligand the intermediate hydrocarbyl complex can be isolated completely free of donor solvents and alkali halides.

Such base-free hydrocarbyls can be easily isolated by recrystallization from hydrocarbon solvents. The last step, i.e. the hydrogenolysis reaction, proceeds under very mild conditions at one atmosphere of hydrogen and ambient temperature. The facile conversion of organolanthanide hydrocarbyls into hydrides in the presence of molecular hydrogen appears to be generally applicable. The three-step procedure outlined above has been successfully carried out with other lanthanide elements.

Important results have been obtained with bifunctional ligands in which tetramethylcyclopentadienyl units are connected by Me_2Si or Me_2Ge [34, 35] units. These compounds, especially the hydrocarbyl and hydride derivatives, show interesting catalytic behavior. They can be regarded as "tied-back" analogues of the $(C_5Me_5)_2Ln$ derivatives. Halides, hydrocarbyls, and hydrides containing these ligands can be synthesized by the methods established in pentamethylcyclopentadienyl chemistry (Scheme 1) [36]

$$LnCl_3 \ + \ Li_2[Me_2Si(C_5Me_4)_2]$$

$$\xrightarrow[\text{- LiCl}]{Et_2O} [Me_2Si(C_5Me_4)_2]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2$$

$$\xrightarrow[\text{- 2 LiCl}]{+\ LiCH(SiMe_3)_2} [Me_2Si(C_5Me_4)_2]LnCH(SiMe_3)_2$$

$$Ln = Nd, Sm, Lu$$

Scheme 1. Preparation of $[Me_2Si(C_5Me_4)_2]LnCH(SiMe_3)_2$

The "tied-back" organolanthanide hydrocarbyls $[Me_2Si(C_5Me_4)_2]NdCH(SiMe_3)_2$, [22] $[Me_2Si(C_5Me_4)(C_5H_4)LuCH(SiMe_3)_2$, (Fig. 3) [37] $[Me_2Ge(C_5Me_4)_2]HoCH(SiMe_3)_2$ [34] and $[Me_2Si(C_5Me_4)\{C_5H_3CH_2CH_2P(tBu)_2\}]ScCH(SiMe_3)_2$ [38] as well as the halide precursors $[Me_2Ge(C_5Me_4)_2]Ln(\mu\text{-}Cl)_2Li(THF)_2$ (Ln = Sm, Lu) [34] and $[Me_2Si\{C_5H_2(tBu\text{-}4)(SiMe_3\text{-}2\}_2]Y(\mu\text{-}Cl)_2Li(THF)_2$ [39] have been structurally characterized, with all hydrocarbyls exhibiting a characteristic γ-C–H–Ln agostic interaction.

In several recent papers Marks and co-workers described the synthesis, structural systematics, absolute configurations, and structural interconversions of a series of C_1-symmetric organolanthanide chloro, alkyl, and amide complexes/precatalysts based on chiral chelating $Me_2Si(C_5Me_4)(C_5H_3R^*)_2$-ligands (= $[Me_2SiCp''(R^*Cp)]^{2-}$), where R^* = (+)-neomenthyl, (−)-menthyl, and (−)-phenylmenthyl [40–42]. These ligands are accessible in three steps starting from known chiral cyclopentadienes (Scheme 2). The synthetic procedure involves metalation of the chiral cyclopentadienes followed by condensation with $Me_4C_5SiMe_2Cl$ and subsequent in situ lithiation to give the corresponding dianions of the chelating ligands.

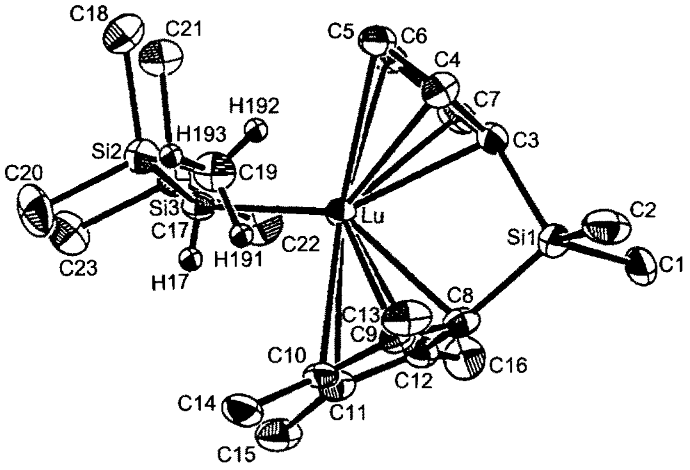
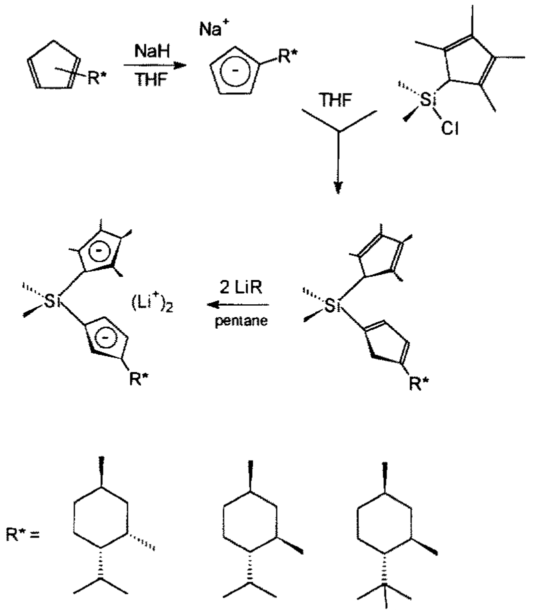


Fig. 3. Molecular structure of $[Me_2Si(C_5Me_4)(C_5H_4)]LuCH(SiMe_3)_2$



Scheme 2. Synthesis of chiral chelating cyclopentadienyl ligands

The lanthanide chloro precursors can be prepared in high yield by transmetalation of the dilithiated ligands with anhydrous lanthanide trichlorides followed by work-up with diethyl ether. Alternatively, the mono-DME adducts can be prepared, Eqs. (7) and (8) [42].

$$\mathrm{Li_2[Me_2SiCp''(R^*Cp)] + LnCl_3}$$

$$\xrightarrow[\text{2. Et}_2\text{O}]{\text{1. THF}} \mathrm{[Me_2SiCp''(R^*Cp)]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2 + LiCl}$$

$R^* =$ (+)-neomenthyl, (−)-menthyl, (−)-phenylmenthyl

$\mathrm{Ln} =$ Y, La, Nd, Sm, Lu (7)

$$\mathrm{Li_2[Me_2SiCp''(R^*Cp)] + LnCl_3}$$

$$\xrightarrow[\text{2. DME}]{\text{1. THF}} \mathrm{[Me_2SiCp''(R^*Cp)]Ln(\mu\text{-}Cl)_2Li(DME) + LiCl} \quad (8)$$

$R^* =$ (+)-neomenthyl, (−)-menthyl

$\mathrm{Ln} =$ Sm, Lu

As established by NMR spectroscopy and circular dichroism, the diastereomerically pure chloro complexes can be epimerized in the presence of donor solvents to afford mixtures of (*R*)- and (*S*)-configurational isomers. The isomer ratio depends on solvent, R^*, and lanthanide ion. Importantly, selective epimerization allowed enrichment in either antipode with diastereomerically pure complexes obtained in a single recrystallization step. This was a crucial prerequisite for the preparation of σ-alkyl or amide precatalysts of desired configuration. The molecular structure of $\mathrm{[Me_2SiCp''\{(+)\text{-}neomenthyl\,Cp\}]Lu(\mu\text{-}Cl)_2Li(Et_2O)_2}$ has been determined by single-crystal X-ray analysis (Fig. 4) [42].

Alkylation or amidation of the chloro complexes affords the corresponding chiral σ-alkyls or amides in high yields Eqs. (9) and (10) [42].

$$\mathrm{[Me_2SiCp''(R^*Cp)]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2 + LiCH(SiMe_3)_2}$$

$$\longrightarrow \mathrm{[Me_2SiCp''(R^*Cp)]LnCH(SiMe_3)_2 + 2\,LiCl} \quad (9)$$

$R^* =$ (+)-neomenthyl, (−)-menthyl, (−)-phenylmenthyl

$\mathrm{Ln} =$ Y, La, Nd, Sm, Lu

$$\mathrm{[Me_2SiCp''(R^*Cp)]Ln(\mu\text{-}Cl)_2Li(Et_2O)_2 + MN(SiMe_3)_2}$$

$$\longrightarrow \mathrm{[Me_2SiCp''(R^*Cp)]LnN(SiMe_3)_2 + LiCl + MCl} \quad (10)$$

$R^* =$ (+)-neomenthyl, (−)-menthyl, (−)-phenylmenthyl

$\mathrm{M} =$ Na, K; $\mathrm{Ln} =$ Y, La, Nd, Sm, Lu

Single crystal structure analyses have been carried out on the complexes (*R*/*S*)-$\mathrm{[Me_2SiCp''\{(+)\text{-}neomenthyl\,Cp\}]YCH(SiMe_3)_2}$, (*R*)-$\mathrm{[Me_2SiCp''\{(-)\text{-}menthyl\,Cp'']SmCH(SiMe_3)_2}$ (Fig. 5), (*R*)-$\mathrm{[Me_2SiCp''\{(-)\text{-}menthyl\,Cp\}]YCH(SiMe_3)_2}$, (*S*)-$\mathrm{[Me_2SiCp''\{(+)\text{-}neomenthyl\,Cp\}]SmN(SiMe_3)_2}$, (*S*)-$\mathrm{[Me_2SiCp''\{(-)\text{-}menthyl\,Cp\}]SmN(SiMe_3)_2}$, and (*R*)-$\mathrm{[Me_2SiCp''\{(-)\text{-}menthyl\,Cp\}]YN(SiMe_3)_2}$. These σ-alkyl and amide complexes are configurationally stable in toluene at 60 °C for many hours. Rapid hydrogenolysis of the hydro-

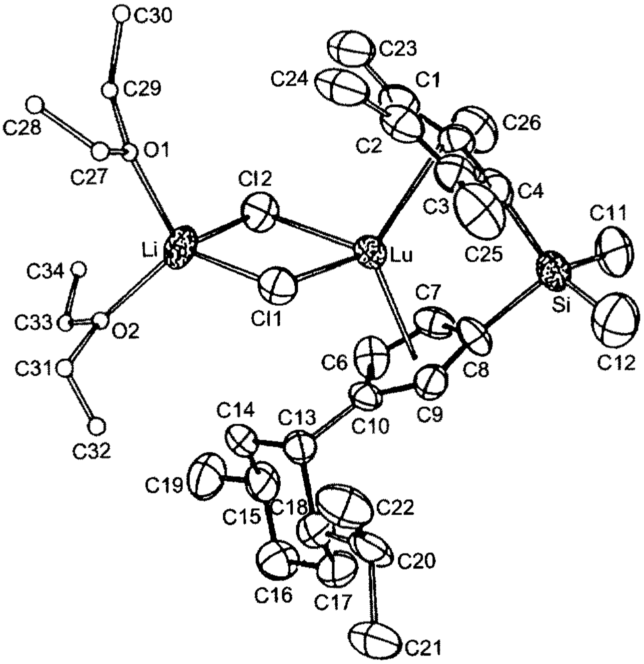


Fig. 4. Molecular structure of [Me_2SiCp''\{(+)-neomenthylCp\}]Lu(μ-Cl)$_2$Li(Et_2O)$_2$

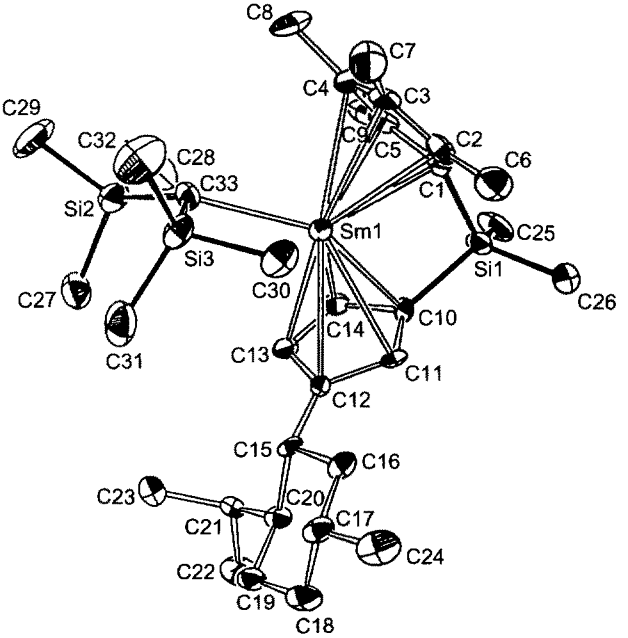


Fig. 5. Molecular structure of (*R*)-[Me_2SiCp''\{(−)-menthylCp\}]SmCH($SiMe_3$)$_2$

carbyl complexes at ambient temperature affords the corresponding hydrides with retention of configuration [42].

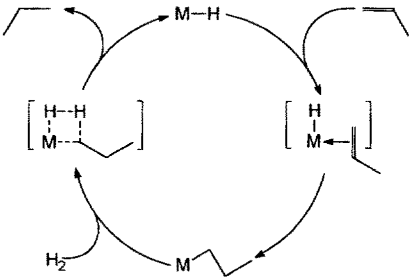
The chiral organolanthanides have been especially designed for asymmetric catalysis. Thus far several enantioselective olefin transformations (hydrogenation, hydroamination/cyclization, hydrosilylation) as well as the polymerization of methyl methacrylate mediated by these chiral organolanthanide metallocenes have been investigated.

3 Olefin Transformations

The most thoroughly investigated group of organolanthanide-catalyzed reactions are monoolefin transformations. These include the following processes: *a*) hydrogenation, *b*) oligomerization, *c*) polymerization, *d*) hydroamination, *e*) hydrosilylation, and *f*) hydroboration, which will be discussed in the above order.

3.1 Hydrogenation

The first lanthanide catalyst for the hydrogenation of ethylene was prepared from a samarium/magnesium alloy. $SmMg_3$ reacts with anthracene in THF solution to give a complex of unknown structure. This intermediate absorbs hydrogen and is then able to catalyze the hydrogenation of ethylene [3,7]. Catalytic activity in hydrogenation reactions was also observed for the reaction products of lanthanide vapors and alkynes. Although incompletely characterized, these materials are believed to contain Ln–H bonds [7,43,44]. Hydrogenation of olefins and alkynes is also effectively catalyzed by various organolanthanide hydrides [29,45–47] as well as cyclopentadienylytterbium(II) complexes. Extraordinarily high catalytic activity in olefin hydrogenation is displayed by the above-mentioned bis(pentamethylcyclopentadienyl)lanthanide hydrides, $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$. Terminal as well as internal olefins are easily hydrogenated in the presence of these organolanthanide hydrides [22,48]. The catalytic hydrogenation of 1-hexene to *n*-hexane was studied in detail. Increasing catalytic activity was found for the series La < Nd < Sm < Lu and the highest turnover number was $120000\ h^{-1}$. This enormous value can be favorably compared to the activities of well-known transition metal homogeneous catalysts. Turnover numbers are $3000\ h^{-1}$ for $RhCl(PPh_3)_3$ and $6400\ h^{-1}$ for $[(COD)Ir(PCy_3)]PF_6$ under similar reaction conditions (25°C, 1 atm of H_2) [49]. Even higher activities have been reported for the "tied-back" metallocene hydrides $[\{Me_2Si(C_5Me_4)_2\}Ln(\mu\text{-}H)]_2$ [25]. A plausible mechanism for organolanthanide-catalyzed α-olefin hydrogenation is shown in Scheme 3.



Scheme 3. Organolanthanide catalyzed α-olefin hydrogenation

The same mechanism as shown in Scheme 3 has been proposed for the selective hydrogenation of substituted dienes catalyzed by $(C_5Me_5)_2YMe(THF)$. The σ-methyl precatalyst reacts with H_2 to yield the active hydride catalyst and methane [50].

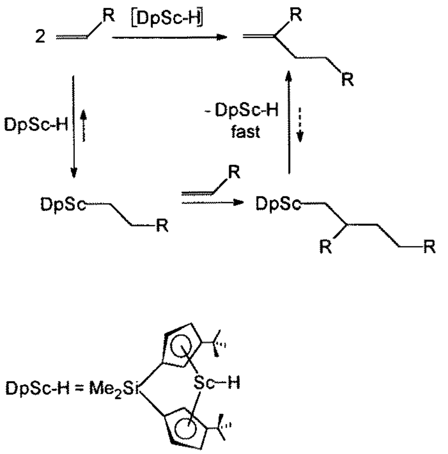
More recently the enantioselective olefin hydrogenation mediated by the chiral organolanthanide metallocenes $[Me_2SiCp''(R^*Cp)]LnCH(SiMe_3)_2$ (R^* = (+)-neomenthyl, (−)-menthyl; Ln = Y, La, Nd, Sm, Lu) has been investigated by Marks et al. [51]. The hydrocarbyl complexes have been found to serve as precatalysts for the effective asymmetric hydrogenation and deuteration of styrene and 2-phenyl-1-butene, respectively. For the samarium-derived catalysts, enantiomeric excesses as high as 64% (96% at −80 °C) and turnover frequencies as high as 26 000 h^{-1} were observed at 25 °C, $P(H_2) = 1$ atm for the hydrogenation of 2-phenyl-1-butene.

3.2 Oligomerization

Several dimerization and oligomerization reactions catalyzed by organolanthanides have been studied. For example, propylene oligomerization was reported to occur in the presence $[(C_5Me_5)_2LuMe]_2$ [9]. Hydrogenolysis of the "tied back" hydrocarbyls $[Me_2Si(C_5Me_4)_2]NdCH(SiMe_3)_2$ (Ln = Nd, Sm, Lu) with H_2 affords the corresponding hydride dimers, which have been shown to oligomerize propylene and 1-hexene [22]. A "tied back" organoscandium hydride has been found to catalyze the dimerization of α-olefins. Head-to-tail dimers are obtained in a highly regiospecific manner (Scheme 4) [52].

3.3 Polymerization

Early mechanistic studies concerning organolanthanide-catalyzed olefin polymerization reactions showed that insertion of the unsaturated hydrocarbon into the lanthanide-carbon σ-bond is a key step. It was first demonstrated for the



Scheme 4. Alkene dimerization with $[Me_2Si(C_5H_3tBu)_2]ScH$

reversible insertion of propylene into the Lu–C bond of methyl-bis(pentamethylcyclopentadienyl)lutetium, Eq. (11) [6, 7].

$$(C_5Me_5)_2LuMe + MeCH{=}CH_2 \leftrightarrow (C_5Me_5)_2LuCH_2CHMe_2 \qquad (11)$$

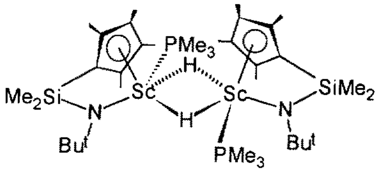
In this sense $[(C_5Me_5)_2LuMe]_2$ can be regarded a model compound for Ziegler-Natta catalysis. The reverse reaction proceeds via β-alkyl elimination. A competing process is β-hydride elimination, which leads to $(C_5Me_5)_2LuH$ dimer and isobutene. On the other hand, $(C_5Me_5)_2LuCH_2CHMe_2$ can be prepared by insertion of isobutene into the lutetium-hydrogen bond [6, 7]. More recent thermochemical studies on the basis of f-element bond enthalpies have shown that insertion of olefins into an Ln–H bond is quite exothermic (ca. 15 kcal mol^{-1}), while β-hydride elimination is less favorable [48].

Very high catalytic activities in the homogeneous polymerization of ethylene are also displayed by $(C_5Me_5)_2ScMe$, $(C_5Me_5)_2NdR$, [53] $(C_5Me_5)_2LaNMe_2$ [54] and the bis(pentamethylcyclopentadienyl)lanthanide hydrides of the type $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ [6, 7, 55–57]. The highest turnover frequency (greater than 1800 s^{-1} at 25°C and 1 atm of ethylene) was reported for $[(C_5Me_5)_2Lu(\mu\text{-}H)]_2$. In a series of important papers Marks and Schumann et al. have compared the behavior of $(C_5Me_5)_2LnCH(SiMe_3)_2$ and $[Me_2Si(C_5Me_4)_2]LnCH(SiMe_3)_2$ ($Ln = La, Nd, Sm, Lu$) as precatalysts in olefin polymerization and hydrogenation reactions [22, 23, 48]. The hydrides $[(C_5Me_5)_2\,Ln(\mu\text{-}H)]$ were shown to be extremely active in olefin polymerization. An even increased activity was found for the "tied back" hydrides $[\{Me_2Si(C_5Me_4)_2\}Ln(\mu\text{-}H)]_2$. In the case of ethylene polymerization polyethylene with a high molecular weight ($M_w = 3.8 - 15 \times 10^5$) and moderate polydispersity ($M_w/M_n = 1.4$–6.4) was produced. The activity of the ethylene polymerization catalysts was found to increase parallel with the ionic radius of the lanthanide metal ($Lu \ll Nd < La$). Propylene and butadiene were not polymerized in the presence of

$[(C_5Me_5)_2Lu(\mu\text{-}H)]_2$ but afforded η^3-allyl complexes via stoichiometric reactions [48].

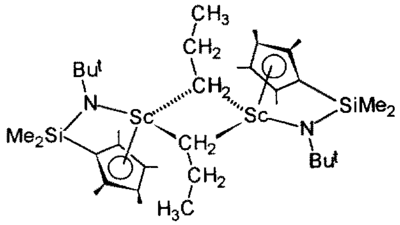
Dimeric yttrium hydrides of the type $[(C_5Me_5)Y(OR)(\mu\text{-}H)]_2$ have been found to catalyze the slow polymerization of 1-hexene to give poly(1-hexene) with $M_w = 15700$ and $M_w/M_n = 1.67$. The active catalyst was proposed to be (μ-H) (μ-hexyl) $[(C_5Me_5)Y(OR)]_2$. The chain propagation proceeds via 1,2-addition and termination via β-hydride elimination [58]. Similar results were obtained with scandium hydrocarbyls and hydrides containing the internally chelating cyclopentadienyl-amide ligand $C_5Me_4SiMe_2N\text{-}t\text{-}Bu^-$ [52, 59]. The dimeric yttrium hydride $[\{rac\text{-}Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}tBuC_5H_2)_2\}Y(\mu\text{-}H)]_2$ has recently been reported to be the first iso-specific single-component α-olefin polymerization catalyst. Using this catalyst highly (97%) isotactic poly(1-olefins) with moderate molecular weights have been manufactured (e.g. poly(1-hexene): $M_w = 24000$ and $M_w/M_n = 1.75$) [39].

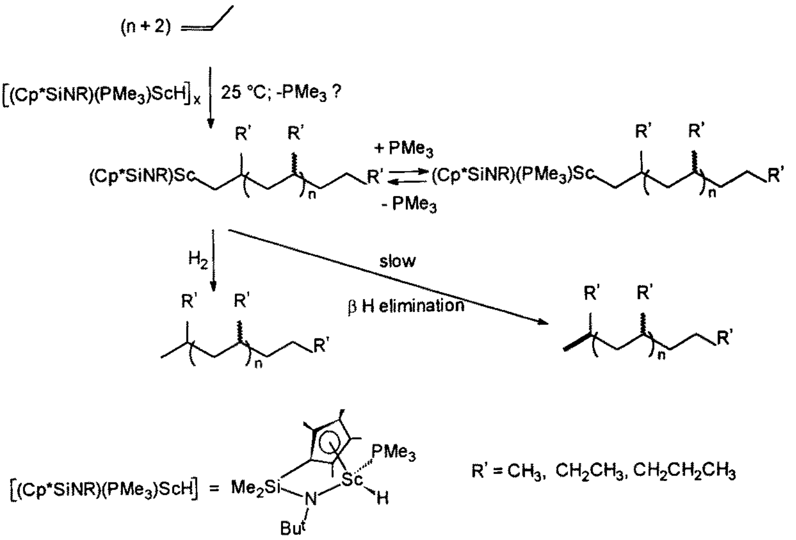
A well-defined, single-component Ziegler-Natta catalyst is the amido-cyclopentadienyl scandium hydride $[(C_5Me_4SiMe_2N\text{-}t\text{-}Bu)Sc(PMe_3)(\mu\text{-}H)]_2$ which was described by Bercaw et al. [60].



The dimeric hydride acts as a single-component, regiospecific polymerization catalyst. It catalyzes the polymerization of α-olefins $RCH = CH_2$ (R = Me, Et, nPr) to polyolefins with $M_w = 4000\text{–}6000$ and $M_w/M_n = 1.7\text{–}2.1$. As in the case of $[(C_5Me_5)Y(OR)(\mu\text{-}H)]_2$ the polymerizations are slow as compared to single-component zirconium catalysts [59]. The proposed mechanism is illustrated in Scheme 5 [52, 60, 61].

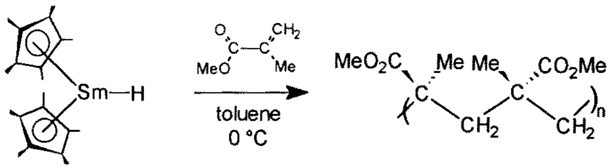
Treatment of $[(C_5Me_4SiMe_2N\text{-}t\text{-}Bu)Sc(PMe_3)(\mu\text{-}H)]_2$ with two equivalents of propylene at low temperature yielded the structurally characterized phosphine-free di-μ-propyl complex $[(C_5Me_4SiMe_2N\text{-}t\text{-}Bu)Sc(\mu\text{-}n\text{Pr})]_2$. This dimeric organoscandium alkyl was found to be an even more active α-olefin polymerization catalyst than the hydride precursor [52].





Scheme 5. α-Olefin polymerization catalyzed by $[(C_5Me_4SiMe_2N\text{-}t\text{-}Bu)Sc(PMe_3)(\mu\text{-}H)]_2$

Polymerization of methyl methacrylate (= MMA) has been effected with the organolanthanide precatalysts $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ and $(C_5Me_5)_2LnMe(THF)$. Both complexes have been found to initiate the living, highly syndiospecific polymerization of methyl methacrylate, Eq. (12) [62].



(12)

Similar activity was reported for the divalent lanthanide organometallics $(MeC_5H_4)_2Yb(DME)$, [63] $(C_5Me_5)_2Yb(THF)_2$, $(C_5Me_5)_2Sm(THF)_2$, and $(C_9H_7)_2Yb(THF)_2$ [64]. The catalytic activity was found to decrease with increasing steric bulk of the cyclopentadienyl ligands ($C_5H_5 > MeC_5H_4 > C_5Me_5$). In the case of samarium it was possible to determine the molecular structure of the active catalyst, $(C_5Me_5)_2Sm[(MMA)_2H]$ (Fig. 6). This intermediate contains an eight membered ring formed by samarium and two MMA molecules. One MMA unit coordinates to the metal in an enolate form and the other one via the carbonyl group. MMA polymerization catalyzed by $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ affords poly(methyl methacrylate) of high molecular weight ($M_w = 55\text{–}563 \times 10^3$) and extremely narrow polydispersity ($M_w/M_n = 1.02\text{–}1.04$) [62, 65].

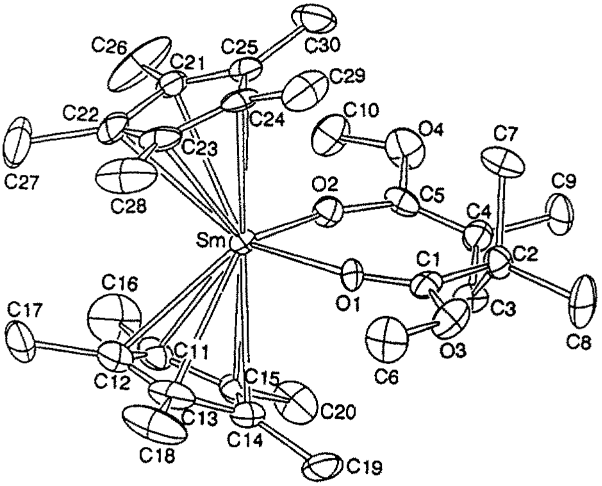
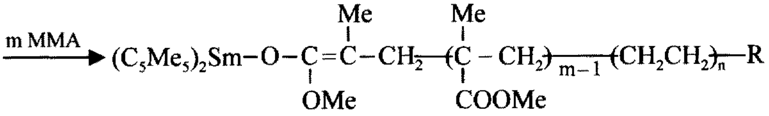


Fig. 6. Molecular structure of $(C_5Me_5)_2Sm[(MMA)_2H]$

The production of syndiotactic poly(methyl methacrylate) was also achieved by using the organolanthanide catalysts $(C_5Me_5)_2LnMe(THF)$ (Ln = Yb,Lu) and $(C_5Me_5)_2Ln(\mu\text{-}Me)_2AlMe_2$ (Ln = Y, Yb, Lu) [64]. Lanthanide catalysts of the type $(C_5Me_5)_2LnR$ (Ln = Sm, Yb, Lu; R = H, Me) also allowed well-controlled block copolymerizations as shown in Eqs. (13) and (14) [62].

$(C_5Me_5)_2Sm{-}(CH_2CH_2)_n{-}R$

R=H, Me

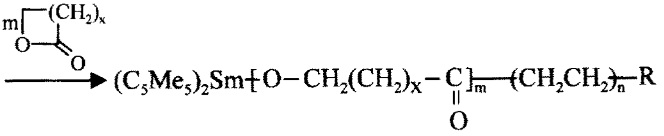


$$\xrightarrow{m\,MMA} (C_5Me_5)_2Sm-O-\underset{OMe}{C}=\overset{Me}{C}-CH_2-(\underset{COOMe}{\overset{Me}{C}}-CH_2)_{m-1}-(CH_2CH_2)_n-R \qquad (13)$$

$(C_5Me_5)_2Sm{-}(CH_2CH_2)_n{-}R$

R=H, Me; x = 3,4

MMA = methyl methacrylate



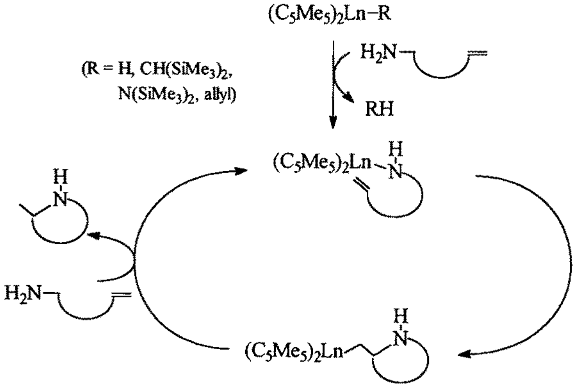
$$\xrightarrow{m\,\text{lactone}} (C_5Me_5)_2Sm[O-CH_2(CH_2)_x-\underset{\overset{\|}{O}}{C}]_m-(CH_2CH_2)_n-R \qquad (14)$$

Recently, chiral organolanthanide metallocenes of the type $[Me_2SiCp''(R^*Cp)]LnCH(SiMe_3)_2$ and $[Me_2SiCp''(R^*Cp)]LnN(SiMe_3)_2$ (R^* = (+)-neomenthyl, (−)-menthyl; Ln = Y, La, Sm, Lu) have been demonstrated to serve as efficient catalysts for the stereoregular polymerization of methyl methacrylate [66]. Stereoregulation, molecular weight, and polydispersity can be controlled by the choice of precatalyst architecture and polymerization conditions. C_1-symmetric catalysts bearing the (+)-neomenthyl chiral auxiliary were found to produce *isotactic* polymers with tacticity increasing with decreasing temperature. In sharp contrast, catalysts bearing the (−)-menthyl substituent produced *syndiotactic* polymers with stereoregularities approaching those of the parent achiral lanthanide metallocenes such as $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.

3.4 Hydroamination

The hydroamination/cyclization of aminoolefins catalyzed by organolanthanides has been studied in great detail by Marks et al. [41, 54, 67, 68]. The catalytic cycle is initiated by formation of an amido complex from $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ or $(C_5Me_5)_2$ LnR and the free amine, followed by intramolecular olefin insertion into the Ln-N bond. The latter step is irreversible and rate limiting. Subsequent protonolysis of the resulting lanthanide hydrocarbyl by the free amine liberates the cyclization product and regenerates the precatalyst $[(C_5Me_5)_2 Ln(\mu\text{-}H)]_2$ (Scheme 6). The active catalytic species was proposed to be $(C_5Me_5)_2Ln\,NHR(H_2NR)$. A model compound, $(C_5Me_5)_2LaNHMe(H_2NMe)$ has been structurally characterized (Fig. 7) [67].

More recently chiral organolanthanide precatalysts of the type $[Me_2SiCp''(R^*Cp)]LnCH(SiMe_3)_2$ and $[Me_2SiCp''(R^*Cp)]LnN(SiMe_3)_2$ (R^* = (+)-neomenthyl, (−)-menthyl; Ln = Y, La, Sm, Lu) have been used for efficient regio- and enantioselective olefin hydroamination/cyclization processes. For example, a > 95% diasteroselectivity at 15 °C was achieved with



Scheme 6. Organolanthanide-catalyzed hydroamination/cyclization of unsaturated amines

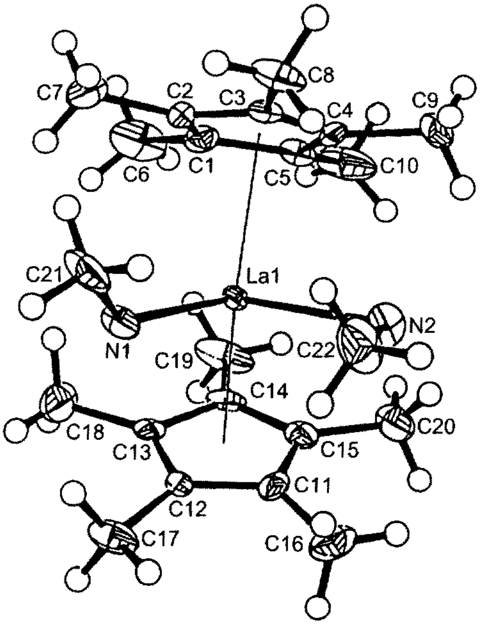
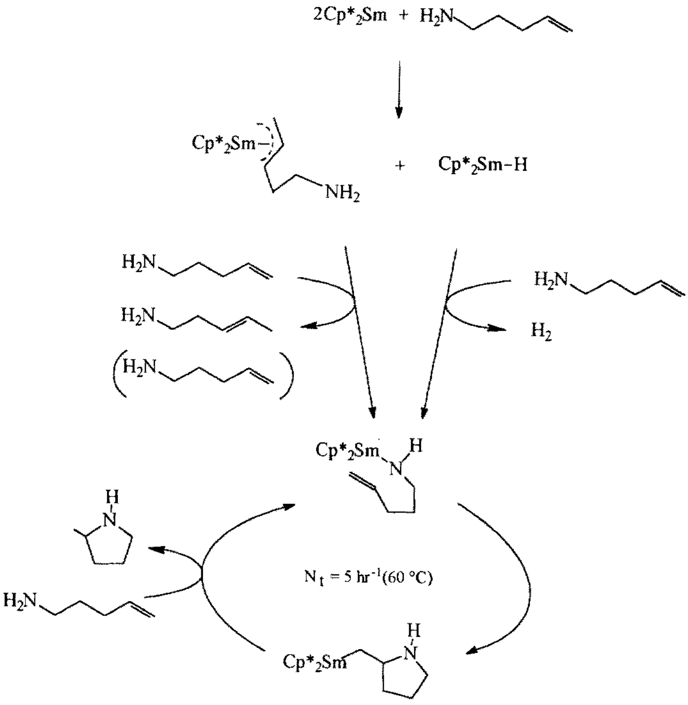


Fig. 7. Molecular structure of $(C_5Me_5)_2LaNHMe(H_2NMe)$



Scheme 7. Hydroamination/cyclization of unsaturated amines catalyzed by $(C_5Me_5)_2Sm$ ($Cp^* = C_5Me_5$)

(+)-neomenthyl precatalysts (Ln = Nd, Sm) for the hydroamination/cyclization of $H_2C{=}CHCH_2CH_2CH(Me)NH_2$ to 2,5-dimethylpyrrolidine [40, 41, 51].

The divalent samarium complexes $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(THF)_2$ have also been found to be effective precatalysts in these hydroamination/cyclization reactions [68]. In this case the initial step is the formation of samarium(III) intermediates via allylic C–H activation [Eq. (15)].

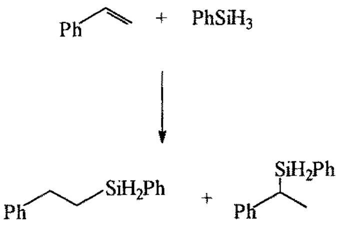
$$\begin{aligned} &2\,(C_5Me_5)_2Sm + CH_2 = CH(CH_2)_3NMe_2 \\ &\quad \rightarrow (C_5Me_5)_2Sm(\eta^3\text{-}H_2CCHCH(CH_2)_2NMe_2) + [(C_5Me_5)_2Sm(\mu\text{-}H)]_2 \end{aligned} \tag{15}$$

Both intermediates can then be protonated by a primary or secondary amine to generate the active catalyst $(C_5Me_5)_2SmNRR'$ (Scheme 7) [68].

A single report on related hydrophosphination reactions of olefins has also appeared in a review article [69].

3.5 Hydrosilylation

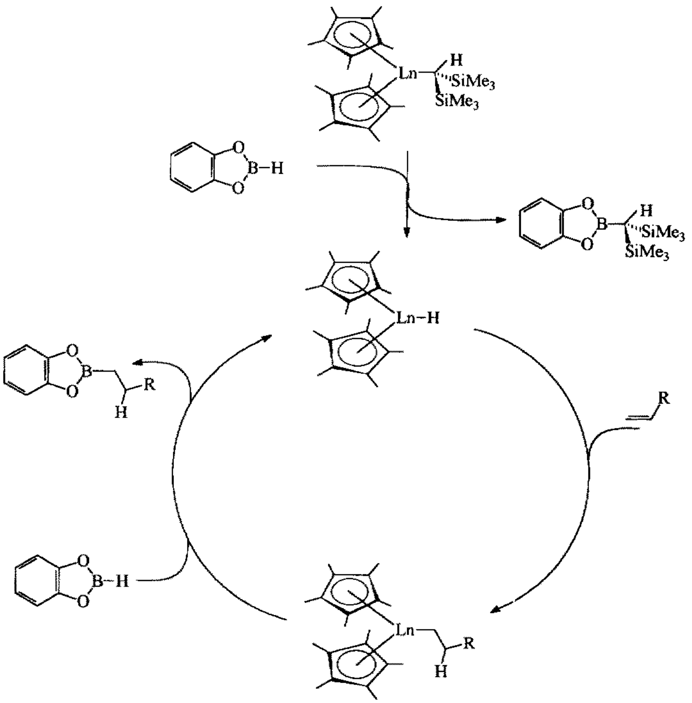
Alkyl complexes of the type $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, Nd) have been reported to catalyze the hydrosilylation of various substituted and functionalized olefines to a mixture of linear and branched products, Eq. (16) [70].



(16)

For yttrium, the hydrocarbyl $(C_5Me_5)_2YCH(SiMe_3)_2$ has been proposed to react with $PhSiH_3$ to give the precatalyst. Further reaction of the intermediate silyl derivative with $PhSiH_3$ affords the active catalyst $[(C_5Me_5)_2Y(\mu\text{-}H)]_2$ besides the coupling product $PhSiH_2SiH_2Ph$ [70].

In addition to achiral precatalysts the chiral lanthanide metallocenes (*R*)-[Me$_2$SiCp″{(−)-menthylCp}]SmCH(SiMe$_3$)$_2$ and (*S*)-[Me$_2$SiCp″{(−)-menthyl Cp}]SmCH(SiMe$_3$)$_2$ have been employed [71]. The hydrocarbyl derivatives have been shown to mediate the enantioselective hydrosilylation of 2-phenyl-1-butene by $PhSiH_3$ with exclusive 1,2-addition and with $N_t \sim 50\,h^{-1}$. In this case enantioselection proceeds with 68% ee ((*R*) product) and 65% ee ((*S*) product) for the (*R*)-Sm and (*S*)-Sm catalysts (70% enantiopure), respectively.



Scheme 8. Organolanthanide-catalyzed hydroboration of olefins

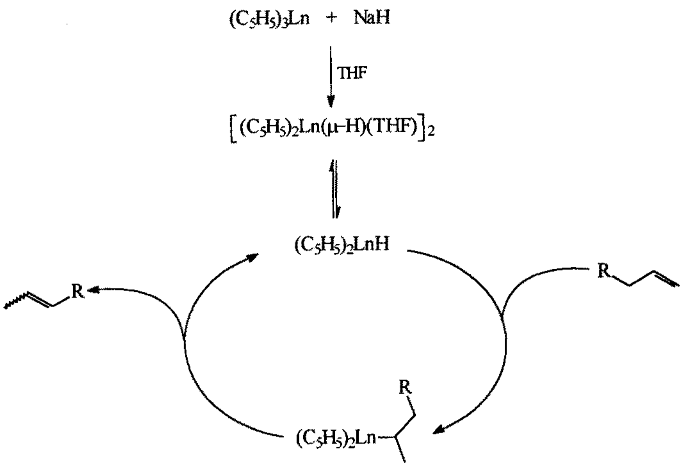
3.6 Hydroboration

Even an organolanthanide-catalyzed variant of the (anti-Markownikoff) hydroboration of olefins has been developed. The catalytic cycle is illustrated in Scheme 8.

Reaction of the precatalyst $(C_5Me_5)_2LnCH(SiMe_3)_2$ with catecholborane produces the active catalyst $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$, together with the corresponding alkylated catecholborane. This is followed by olefin insertion and hydroboration of the intermediate lanthanide alkyl. Conventional oxidative work-up of the resulting alkylated catecholborane affords the alcohol. $(C_5Me_5)_2Sm(THF)_2$ has been found to be another suitable precatalyst [72].

3.7 Miscellaneous Olefin Transformations

Isomerization of terminal olefins was achieved with the system $Ln(C_5H_5)_3/NaH$ ($Ln = Y, Er, Lu$). The reactions were carried out at 45 °C in THF and afforded *cis-* and *trans-*2-alkenes in very good yields. The catalytic isomerization may occur via organolanthanide hydride intermediates. The proposed mechanism is depicted in Scheme 9 [73].

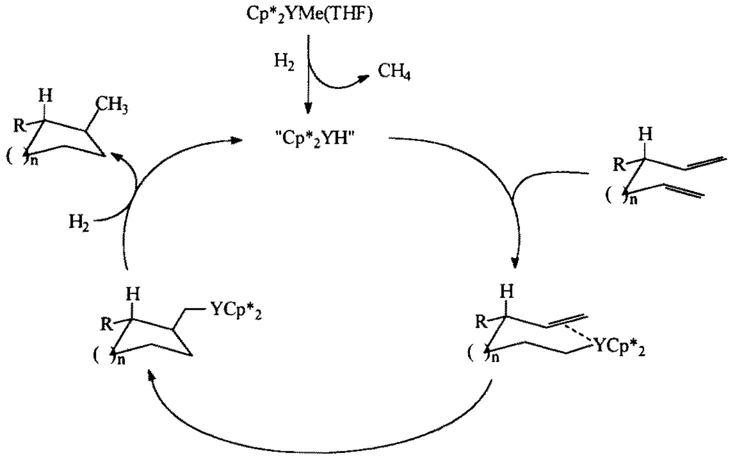


Scheme 9. Organolanthanide-catalyzed isomerization of terminal olefins

4 Diene Transformations

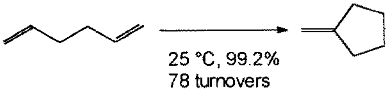
4.1 Cyclization

The catalytic hydrocyclization of 1,5- and 1,6-dienes has been achieved by using $(C_5Me_5)_2YMe(THF)$ as precatalyst. The catalytic species is bis(pentamethylcyclopentadienyl)yttrium hydride, which is formed by C–H-activation and elimination of methane (Scheme 10) [74].



Scheme 10. Organolanthanide-catalyzed hydrocyclization of 1,5- and 1,6-dienes

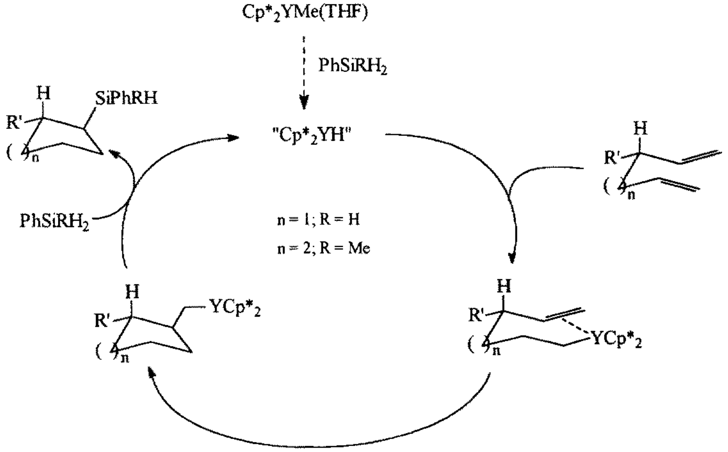
Hydrocyclization of 1,5-hexadiene to methylcyclopentane is also effectively catalyzed by the scandium hydride $[Me_2Si(C_5Me_4)_2]ScH(PMe_3)$, Eq. (17) [52]. The mechanism of this process was investigated by deuteration experiments [75]. A model complex, the pendant phosphine-substituted cyclopentadienyl complex $[Me_2Si(C_5Me_4)\{C_5H_3CH_2CH_2P(tBu)_2\}]ScCH(SiMe_3)_2$, was synthesized in order to study the influence of a high effective phosphine concentration on these scandium-catalyzed processes [38].



(17)

4.2 Hydrosilylation

The organoyttrium species $(C_5Me_5)_2YCH(SiMe_3)_2$ has been demonstrated to effectively catalyze the selective hydrosilylation (i.e. the addition of phenylsilane) of the less substituted olefin site in a diene substrate [76]. More recently an organoyttrium-catalyzed sequential cyclization/silylation reaction of 1,5-dienes and 1,6-dienes was developed by Molander et al. (Scheme 11) [27]. In this study the easily accessible σ-methyl complex $(C_5Me_5)_2YMe(THF)$ has been shown to be an efficient catalyst for the annulation and subsequent silylation of substituted 1,5- and 1,6-dienes. The reaction tolerates a variety of functional groups and proceeds with excellent yields and diastereoselectivities. Interestingly, this reaction takes precedence over the dehydrogenative polymerization of the silanes, which has previously been reported to be a remarkably facile process (cf. Sect 6.2.).



Scheme 11. Organoyttrium-catalyzed sequential cyclization/silylation of 1,5- and 1,6-dienes

4.3 Polymerization

Mono(cyclopentadienyl) and mono(indenyl)lanthanide dichlorides have been used as catalysts for the polymerisation of butadiene, and the kinetics have been studied [77–79]. Aluminum alkyls have been used as co-catalysts. In the case of $(C_5H_5)LnCl_2$ the activity in catalyzing the stereospecific polymerization of butadiene to *cis*-1,4-polybutadiene decreased in the order $Nd > Pr > Y > Ce > Gd$ [79]. The novel mono(cyclopentadienyl)-tris(allyl) lanthanate(III) complexes $[Li(dioxane)_2][Cp'La(\eta^3\text{-}C_3H_5)_3]$ ($Cp' = C_5H_5$, $C_5Me_5, C_9H_7, C_{13}H_9$) catalyze the polymerization of butadiene in toluene under standard conditions with moderate activity and a high trans-selectivity [80]. Highly active catalysts for the production of cis-1,4-polybutadiene are formed by combining tris(2,4-dimethylpentadienyl)neodymium, $Nd(2,4\text{-}C_7H_{11})_3$, with Lewis acids such as $SnCl_4$, $SnPh_2Cl_2$, $AlEtCl_2$, or $AlBr_3$. An active precatalyst in this system, hexanuclear $Nd_6Cl_{12}(2,4\text{-}C_7H_{11})_6(THF)_2$ has been isolated and structurally characterized. In this unusual cluster compound two hexagonal bipyramidal Nd_3Cl_5 units are connected via two chloro bridges. The pentadienyl ligands are coordinated to neodymium in a pentahapto fashion [81].

5 Alkyne Transformations

5.1 Oligomerization

One of the first results reported in this area was the finding that diphenylacetylene is dimerized in the presence of tris(cyclopentadienyl)samarium [22]. The lanthanide hydrocarbyls $(C_5Me_5)_2LnCH(SiMe_3)_2$ ($Ln = Y, La, Ce$) have been shown to be precatalysts in the oligomerization of terminal alkynes $RC{\equiv}CH$ [82]. The catalytically active species are the acetylide derivatives $(C_5Me_5)_2LnC{\equiv}CR$. Solvated acetylides $(C_5Me_5)_2LnC{\equiv}CR(L)$ ($L = THF, Et_2O$) have been isolated for Ln = Y, Ce, Sm, and the samarium complex $(C_5Me_5)_2SmC{\equiv}CPh(THF)$ has been structurally characterized (Fig. 8) [33].

The ionic radius of the lanthanide metal significantly influences the nature of the products. For example, with the larger lanthanides La and Ce higher oligomers (preferably trimers) are formed. In the case of Ln = Y the products are generally dimers, but the regioselectivity depends on the substituent R. The dimers $RHC{=}C(H){-}C{\equiv}CR$ are obtained with $R = Ph$ or $SiMe_3$. With bulky substituents ($R = i$Pr, tBu) the result is a head-to-tail dimerization of the terminal alkyne, Eq. (18) [82].

$$2RC{\equiv}CH \rightarrow H_2C{=}C(R){-}C{\equiv}CR \qquad (18)$$

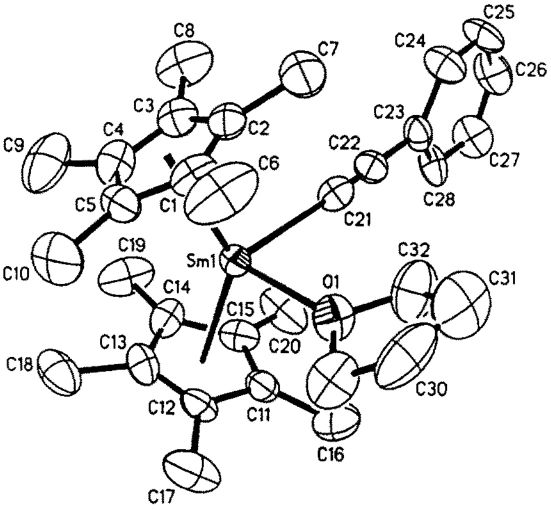
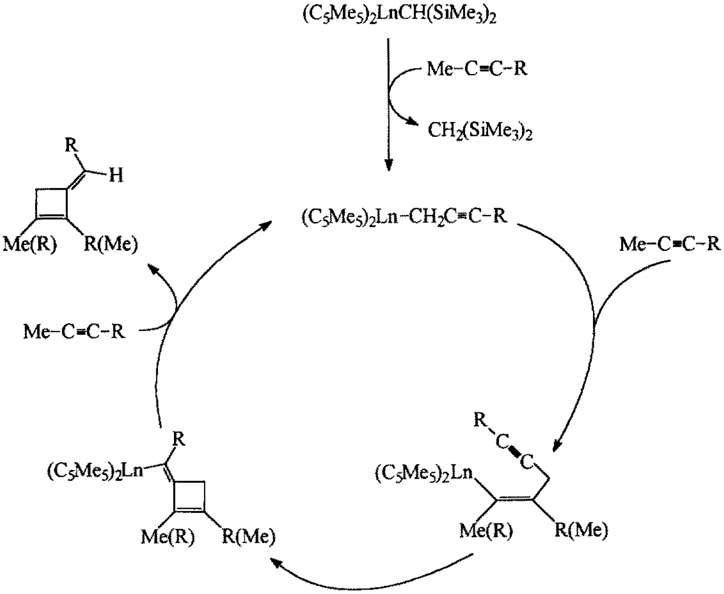


Fig. 8. Molecular structure of $(C_5Me_5)_2SmC{\equiv}CPh(THF)$

Alkynes of the type $MeC{\equiv}CR$ (R = Me, Et, *n*Pr) are cyclodimerized in the presence of $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = La, Ce) to afford 3-alkylidene-cyclobutenes [82]. In this case the active catalyst is $(C_5Me_5)_2Ln\text{-}CH_2C{\equiv}CR$, which is formed by C–H activation upon reaction of the alkyne with the precatalyst $(C_5Me_5)_2LnCH(SiMe_3)_2$. The proposed mechanism is illustrated in Scheme 12.

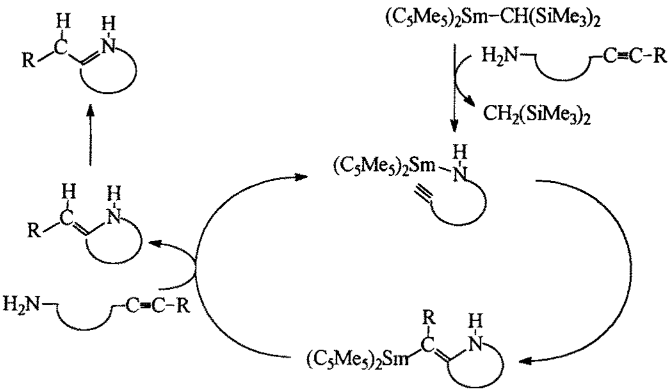


Scheme 12. Organolanthanide-catalyzed cyclodimerization of alkynes

Steric factors strongly influence the outcome of this reaction. Presumably for steric reasons, isolated $(C_5Me_5)_2YCH_2C{\equiv}CR$ has been found inactive towards $MeC{\equiv}CMe$. In the case of sterically more demanding R substituents only C–H activation of the α-methyl group is observed and the reaction stops at the stage of precatalyst formation [83].

5.2 Hydroamination

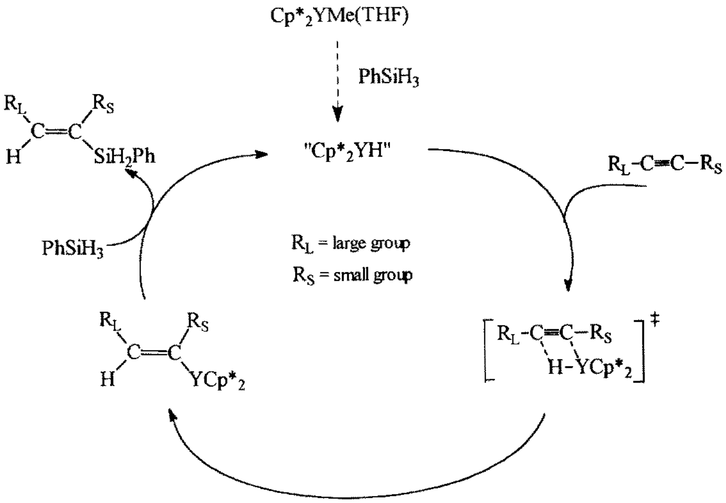
A recent extension of the thoroughly studied organolanthanide-catalyzed olefin hydroamination (cf. Section 2.4.) involves the use of amino-substituted alkynes as substrates. The organolanthanide complex $(C_5Me_5)_2SmCH(SiMe_3)_2$ serves as precatalyst for the efficient and regiospecific hydroamination/cyclization of aliphatic and aromatic aminoalkynes $RC{\equiv}C(CH_2)_nNH_2$ to yield the corresponding heterocycles (Scheme 13). The turnover-limiting step is the intramolecular alkyne insertion into the Sm–N bond which is followed by rapid protonolysis of the resulting Sm–C bond [84].



Scheme 13. Organosamarium-catalyzed hydroamination and cyclization of aminoalkynes

5.3 Hydrosilylation

The readily available yttrocene derivative $(C_5Me_5)_2YMe(THF)$ has been shown to be an effective catalyst for the hydrosilylation of internal alkynes [85]. A single stereoisomer, i.e. the product of *cis* addition of phenylsilane to the alkyne, is formed in the reaction with symmetrically substituted alkynes. Comparable reactions with a variety of unsymmetrically substituted internal alkynes resulted in a regioselective hydrosilylation reaction in which the silane moiety is placed at the sterically less hindered carbon atom of the alkyne. Various functional groups such as halides, amines, protected alcohols, and trisubstituted olefins are tolerated by the reaction conditions with no decrease of the yield. Instead of the σ-methyl complex $(C_5Me_5)_2YCH(SiMe_3)_2$ can also be used as the precatalyst. The proposed catalytic cycle for these reactions is shown in Scheme 14. The scenario is initiated by formation of "$(C_5Me_5)_2YH$" via σ-bond metathesis between $(C_5Me_5)_2YMe(THF)$ and $PhSiH_3$. The monomeric organoyttrium hydride serves as the active catalyst. This is followed by insertion of the alkyne into the Y–H bond. The resulting σ-alkenyl species can then react with phenylsilane through a σ-bond metathesis reaction to release the alkenylsilane product and finally regenerate the catalytically active hydride species.



Scheme 14. Selective hydrosilylation of internal alkynes catalyzed by $(C_5Me_5)_2YMe(THF)$

6. Other Organolanthanide-Catalyzed Reactions

6.1 Polyester Formation

Ring opening polymerization of lactones has been achieved with various bis(cyclopentadienyl)lanthanide halides as catalysts. For example, polymerization of ε-caprolactone in the presence of $(C_5H_5)_2YCl(THF)$ afforded polycaprolactone with $M_w = 125000$ and $M_w/M_n = 1.78$ [86]. A variety of samarium(II) complexes have also been shown to catalyze the ring-opening polymerization of ε-caprolactone [87]. A wide range of aldehydes are efficiently dimerized to the corresponding esters by catalytic amounts of $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Nd, La). This reaction led to a new organolanthanide-catalyzed synthesis of polyesters from dialdehydes [88].

6.2 Miscellaneous Reactions

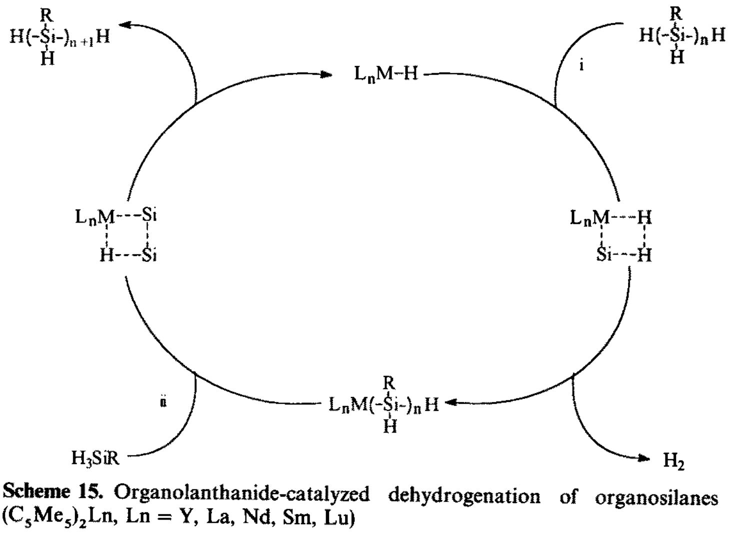
The dimeric hydride species $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ and $[\{Me_2Si(C_5Me_2)_2\}Nd(\mu\text{-}H)]_2$ have been reported to catalyze the isomerization of (*E*)-*N*, *N*-dimethyl-3-phenyl-2-butenylamine to (*E*)-*N*, *N*-dimethyl-3-phenyl-1-butenylamine at 80 °C in C_6D_6 [42].

Catalytic hydrogenation of the cyanide function in *t*-butylcyanide to afford neopentylamine has been achieved with $[(C_5Me_5)_2ScH]_n$, Eq. (19) [52].

$$t\mathrm{BuC{\equiv}N} \xrightarrow{[(C_5Me_5)_2ScH]_n} t\mathrm{BuCH_2NH_2} \tag{19}$$

An interesting catalytic application of $[(C_5Me_5)_2Sc(\mu\text{-}D)]_n$ originated from the observation, that this compound undergoes intramolecular H/D exchange reaction with the C_5Me_5 methyl groups [89]. Subsequently it was discovered, that $[(C_5Me_5)_2Sc(\mu\text{-}H)]_n$ catalyzes the preparation of high isotopic purity $C_5(CD_3)_5H$ from pentamethylcyclopentadiene. The deuteration is conducted under a D_2 atmosphere in C_6D_6 at 145 °C [90].

Organolanthanides have been found to catalyze the dehydrogenation of organosilanes $RSiH_3$ to give polyorganosilanes [70, 91, 92]. The latter are of practical interest as precursors for silicon carbide ceramics. Scheme 15 illustrates the proposed catalytic cycle. Precatalysts are the lanthanide hydrocarbyls $(C_5Me_5)_2LnCH(SiMe_3)_2$ (Ln = Y, La, Nd, Sm, Lu), while the active catalyst is thought to be the corresponding hydride $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$. The rate law for the dehydrogenative coupling of monoorganosilanes is $[(C_5Me_5)_2LnCH(SiMe_3)_2]^1\,[RSiH_3]^1$. As found earlier for organolanthanide-catalyzed olefin hydrogenation, [70] the relative rates parallel the ionic radii of the lanthanide elements and increase in the order La < Nd < Sm < Y < Lu [91].



Scheme 15. Organolanthanide-catalyzed dehydrogenation of organosilanes $RSiH_3$ (L_nM = $(C_5Me_5)_2Ln$, Ln = Y, La, Nd, Sm, Lu)

$(C_5Me_5)_2SmCH(SiMe_3)_2$ was recently found to catalyze the formation of low molecular weight oligostannanes from $n\mathrm{Bu}_2SnH_2$ [93].

7 Concluding Remarks

Within the past ten years several classes of lanthanide metallocenes, especially hydrocarbyl and hydride derivatives, have turned into highly valuable homogeneous catalysts. In most cases the organolanthanide precatalysts are isolable, well-defined species. Especially a variety of olefin transformations is effectively and selectively catalyzed by lanthanide metallocenes. The organolanthanide-mediated reactions include hydrogenation, oligomerization, polymerization, isomerization, hydroamination, hydrosilylation, hydrophosphination, hydroboration and reductive cyclization. Organolanthanide metallocenes combine several favorable characteristics such as extremely rapid kinetics and very high catalytic activities. In addition, the series of lanthanide elements offers unique opportunities for tuning catalyst properties depending on ionic radii and ancillary ligand architecture. Low costs as compared to the platinum group metals and the lack of heavy-metal toxicity add to the increasing attractivity of lanthanide metallocene catalysts. Thus research focused on organolanthanides in homogeneous catalysis is anticipated to grow at a rapid pace.

8 References

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