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# Intramolecular coordination in Group 3 and lanthanide chemistry. An overview [1]

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**Contents**



**Abstract**

The presence of potentially intramolecularly coordinating substituents in ligands can be an attractive alternative to steric bulk as an approach to stabilizing monomeric, solvent-free complexes of Lewis-acidic metal complexes. In addition, intramolecular coordination has proven to be a useful tool for the preparation of well-defined mixed-metal complexes. This paper gives an overview of the various types of ligands containing intramolecularly coordinating substituents that have been used in complexes with Group 3 and lanthanide metals. Emphasis is put on the synthesis of such complexes and on an analysis of the intramolecular

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[1] Dedicated to Kees Vrieze on the occasion of the 25th anniversary of his professorship at the University of Amsterdam. This overview covers the literature until February 1995.


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coordination present. Their (potential) applications as catalysts in organic transformations and as precursors for lanthanide-oxide-containing ceramics are described.

*Keywords:* Lewis-acidic metal complex; Intramolecular coordination; Ceramic; Group 3; Lanthanides

## 1. Introduction

The general interest in monomeric, solvent- and salt-free complexes of the lanthanides can be seen as a result of two separate lines of research. Firstly, in order to take full advantage of the Lewis-acidic properties of the lanthanide ions for organic transformations and/or catalysis, the lanthanide complexes should preferably be monomeric, solvent-free and contain available coordination sites. Secondly, lanthanide complexes that are to be used as precursors for lanthanide-oxide-containing ceramics that are prepared via metal–organic chemical vapor deposition (MOCVD) should preferably be monomeric and salt-free in order to obtain optimal vapor pressures.

One approach to prevent association of metal complexes is to introduce sterically bulky substituents on the ligands. For example, while lanthanide alkoxides[2] and phenolates are typically polymeric in structure [2], monomeric, solvent-free complexes have been reported that use sterically demanding monoanionic ligands like $OCMeEt^iPr$ [3] and $OC_6H_2$-$^tBu_2$-2,6-Me-4 [4]. An attractive alternative to this approach is the introduction of potentially intramolecularly coordinating substituents on the ligands. When these substituents coordinate to the metal center, they combine steric shielding of the metal center with electron donation to the metal center. The latter reduces the Lewis acidity of the metal center and, in combination with the shielding effect, may prevent association of the complexes, and also retention of salt or donor molecules at the metal center. When the donor substituents are pendant, they still provide steric shielding of the metal center. These pendant substituents can also serve as Lewis basic functional groups and add reactivity to the complex or serve as anchoring places for other metal complexes. This last option, which was recently also put forward by Anwander et al. [5], can be of great value in, for example, the preparation of heterometallic catalysts or heterometallic precursors for high-temperature superconductors [6].

During the last 15 years there has been an increase in the interest in potentially intramolecularly coordinating substituents in combination with the Lewis-acid lanthanide ions. The following paragraphs give an overview of the literature concerning this subject.

## 2. Cyclopentadienyl-based ligands (Table 1)

Only in the last decade has attention been focused on donor-substituted derivatives of the cyclopentadienyl ligand, which is traditionally used in lanthanide chemistry.

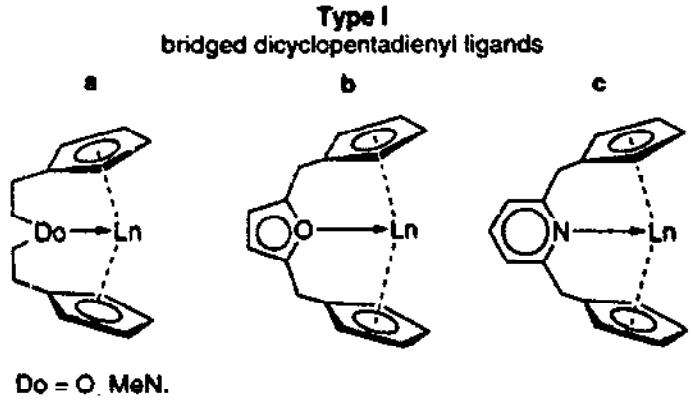
[2] For a review on lanthanide alkoxide chemistry up to 1990, see Ref. [1].

Table 1
Lanthanide complexes of cyclopentadienyl-based ligands containing intramolecularly coordinating substituents

| | Complex | Lanthanide metals[a] | Ln–Do bond lengths (Å) | Ligand type | Ref. |
|---|---|---|---|---|---|
| 1 | $[O(CH_2CH_2C_5H_4)_2]LnCl$ | Y, Nd, Gd, Ho, Er, Yb, Lu | — | Ia | [7] |
| 2 | $[O(CH_2CH_2C_5H_4)_2]Ln(C_5H_4)$ | Y, Nd, Gd, Er, Yb, Lu | — | Ia | [14] |
| 3 | $[O(CH_2CH_2C_5H_4)_2]Ln(C_5H_3Me)$ | Y, Yb | — | Ia | [14] |
| 4 | $\{[O(CH_2CH_2C_5H_4)_2]LnH\}_2$ | Y, Gd, Er, Yb, Lu | — | Ia | [12] |
| 5 | $[O(CH_2CH_2C_5H_4)_2]Ln(N_2C_3HMe_2)$ | Y, Lu | — | Ia | [13] |
| 6 | $\{[O(CH_2CH_2C_5H_4)_2]Ln\}_2(N_2C_3HMe_2)(OH)$ | Y, Lu | Y–O: 2.662(4)<br>Lu–O: 2.667(7) | Ia | [13] |
| 7 | $\{[C_4H_2O(CH_2C_5H_4)_2\text{-}2,5]LnCl\}_2$ | Y, Nd, Sm, Yb | — | Ib | [15] |
| 8 | $\{[C_4H_2O(CH_2C_5H_4)_2\text{-}2,5]LnH\}_2$ | Y, Nd, Sm, Yb | — | Ib | [15] |
| 9 | $\{[MeN(CH_2CH_2C_5H_4)_2]LnCl\}_2$ | Y, Nd, Sm, Yb | — | Ia | [16] |
| 10 | $\{[C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]LnCl\}_2$ | Y, Pr, Nd, Sm, Dy, Er, Yb, Lu | — | Ic | [17] |
| 11 | $[C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]_3Ln_2$ | Pr | — | Ic | [17] |
| 12 | $[(MeOCH_2CH_2C_5H_4)_2LnCl]_2$ | La, Pr, Nd | La–O: 2.666(2), 2.775(2) | II | [18] |
| 13 | $(Me_2NCH_2CH_2C_5H_4)_2LnCl$ | Nd, Lu | Nd–N: 2.804(2), 2.772(2) | II | [19, 20] |
| 14 | $(MeOCH_2CH_2C_5H_4)_2LnI$ | Y, La, Yb | Y–O: 2.47(2), 2.49(2)<br>La–O: 2.583(11), 2.584(11)<br>Yb–O: 2.436(12), 2.464(11) | II | [21, 22] |
| 15 | $(MeOCH_2CH_2C_5H_4)_2LnBH_4$ | La, Pr, Nd, Sm, Gd | Pr–O: 2.605(8), 2.605(8)<br>Nd–O: 2.553(13), 2.566(17) | II | [23] |
| 16 | $[(MeOCH_2CH_2C_5H_4)_2LnH]_2$ | Y, La, Pr, Ho | Y–O: 2.462(5), 2.458(4)[b] | II | [24] |
| 17 | $[(MeOCH_2CH_2C_5H_4)_2Ln(OH)]_2$ | Ho | Ho–O: 2.538(2) | II | [24] |
| 18 | $[(MeOCH_2CH_2C_5H_4)_2Ln(THF)]^+[Co(CO)_4]^-$ | Sm, Yb | Yb–O: 2.41(1), 2.41(1) | II | [25] |
| 19 | $(MeOCH_2CH_2C_5H_4)_3Ln$ | La, Nd, Pr | Pr–O: 2.740(3), 2.836(3)<br>Sm–O: 2.744(3), 2.923(4) | II | [19, 26] |
| 20 | $(Me_2NCH_2CH_2C_5H_4)_3Ln$ | La, Nd | La–N: 2.898(6), 3.688(5)<br>Nd–N: 2.73(1) | II | [20] |
| 21 | $(MeOCH_2CH_2C_5H_4)_2Ln$ | Sm, Yb | Yb–O: 2.564(3), 2.564(3)[c] | II | [27] |
| 22 | $(Me_2NCH_2CH_2C_5H_4)_2Ln$ | Sm | — | II | [28] |
| 23 | $[C_5H_4N\text{-}2\text{-}(CH_2)_nCMe_2C_5H_4]_2Ln$ | Yb | Yb–N: 2.494(7), 2.469(7) [$n=0$] | II | [29] |
| | $[C_5H_4N\text{-}2\text{-}(CH_2)_nCMe_2C_5H_3SiMe_3]_2Ln$ | Yb | Yb–N: 2.462(15), 2.470(13) [$n=1$] | II | |
| 24 | $[(C_5H_5)Fe(C_5H_3CH_2NMe_2)]_3Ln\cdot LiCl\cdot THF$ | Ce, Pr, Nd | — | III | [30] |
| 25 | $[(C_5H_5)Fe(C_5H_3CH_2NMe_2)]_3Ln$ | Yb | — | III | [30] |
| 26 | $[(C_5H_5)Fe(C_5H_3CH_2NMe_2)]_2LnCl$ | La | — | III | [30] |
| 27 | $(C_5H_5)_2Ln[(C_5H_5)Fe(C_5H_3CH_2NMe_2)]\cdot(THF)_n$ | Sm ($n=1$), Er ($n=0$) | — | III | [30] |
| 28 | $(C_5H_5)Ln[(C_5H_5)Fe(C_5H_3CH_2NMe_2)]_2$ | Yb | — | II | [30] |

[a] Underlining indicates that a crystal structure is available. [b] Two crystallographically inequivalent molecules. [c] X-Ray structure of THF-adduct.

This attention has been partly academic (stabilization of low coordination numbers) and partly directed towards the stabilization of hydride species that are of interest with respect to catalytic hydrogenation reactions.




### 2.1. Complexes of bridged dicyclopentadienyl ligands

The first complexes of type I to be synthesized were the monomeric monochloride complexes $[O(CH_2CH_2C_5H_4)_2]LnCl$ (1; Ln is Y, Nd, Gd, Ho, Er, Yb, Lu) [7], which were prepared by reaction of $LnCl_3$ with one equivalent of $[O(CH_2CH_2C_5H_4)_2]Na_2$ at −20°C in THF. These complexes were reported to be much more stable towards air and moisture than the corresponding $Cp_2LnCl$ [8] (Cp is $C_5H_5$) and $[CH_2(CH_2CH_2C_5H_4)_2]LnCl$ [9] complexes. Evidence for coordination of the oxygen functionality to the lanthanide centers was obtained from IR measurements, which show a shift of the C O C stretching vibration to lower frequency relative to that in the starting disodium complex $[O(CH_2CH_2C_5H_4)_2]Na_2$. In addition, XPS measurements showed a decrease in the binding energies of the lanthanide atoms, while the binding energies of oxygen increase, consistent with coordination of oxygen to the lanthanide centers. In combination with NaH, $[O(CH_2CH_2C_5H_4)_2]YCl$ was shown to be an effective catalyst for the hydrogenation of hexenes at 45°C under 1 atm of $H_2$. The activity decreased in the order 1-hexene > 2-hexene ≫ cyclohexene, but the complex was more reactive than $Cp_2YCl$ and required a smaller excess of NaH [10].

Substitution of chloride by cyclopentadienyl [11], hydride [12] and 1,3-dimethylpyrazolate [13], using the corresponding sodium reagents in THF, has been reported for these complexes. For the cyclopentadienyl complexes $[O(CH_2CH_2C_5H_4)_2]Ln(C_5H_3R)$ (2: R is H, Ln is Y, Nd, Gd, Er, Yb, Lu; 3: R is Me, Ln is Y, Yb), $\eta^5$-coordination of the cyclopentadienyl was deduced from NMR and IR data for the complexes, as well as from their lack of reactivity towards $CCl_4$ (the latter selectively attacks $[CH_2(CH_2C_5H_4)_2]Ti(\eta^1\text{-}C_5H_5)_2$ to give $[CH_2(CH_2C_5H_4)_2]TiCl_2$ [14]).

The dimeric hydride complexes $\{[O(CH_2CH_2C_5H_4)_2]Ln(\mu\text{-}H)\}_2$ (4; Ln is Y, Gd, Er, Yb, Lu) [12] are very sensitive towards air and moisture, soluble in THF, but insoluble in hydrocarbons at room temperature. These complexes react with 1-hexene to give the corresponding hexyl complexes, which can subsequently be hydrolyzed

to give hexane. The yield of hexane was found to depend on the reaction temperature, the concentration of the hydrides and on the lanthanide metal. In addition, the yield of hexane increased dramatically on the addition of a fourfold excess of NaH [12]. The hydride complexes **4** also react with the (acidic) hydrogen of terminal alkynes with formation of the corresponding alkynide complex and $H_2$ [12]. The system $\{[O(CH_2CH_2C_5H_4)_2]YH\}_2$/NaH (1:20 molar ratio) effectively reduces organic halides, with the rate depending on the position of the halogen atom (*p*-bromotoluene > *m*-bromotoluene > *o*-bromotoluene) as well as on the bond energy of the C–X bond (R–I > R–Br ≫ R–Cl, R–F). This system is also able to reduce organic bromides catalytically [12].

The 1,3-dimethylpyrazolate complexes $[O(CH_2CH_2C_5H_4)_2]Ln(N_2C_3HMe_2)$ (**5**; Ln is Y, Lu) are highly sensitive towards air and moisture, and the products of their partial hydrolysis $[O(CH_2CH_2C_5H_4)_2]Ln(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)Ln[O(CH_2CH_2C_5H_4)_2]$ (**6**; Ln is Y, Lu) were the first complexes of type **I** to be crystallographically characterized. The X-ray structures of these two complexes show nine-coordinate yttrium and lutetium centers as a result of intramolecular coordination of the oxygen functionality to the metal [13].

With a furyl moiety bridging the two cyclopentadienyl ligands (**Ib**), the dimeric complexes $\{[C_4H_2O(CH_2C_5H_4)_2\text{-}2,5]Ln(\mu\text{-}Cl)\}_2$ (**7**; Ln is Y, Nd, Sm, Yb) [15] were obtained, following a synthetic procedure similar to that used for complexes **1**. These air- and moisture-sensitive complexes decompose on heating before sublimation. Efforts to obtain similar complexes for the early lanthanides La and Pr were unsuccessful. The dimeric nature of the complexes follows from their mass spectra, and may be ascribed to the somewhat shorter ring-bridging linker in **Ib** as compared to **Ia**. This leads to a smaller bite angle for the dicyclopentadienyl ligand. Proof for intramolecular coordination of the furyl oxygen to the lanthanide metals was obtained from IR and XPS measurements. The complexes were transformed in situ to the corresponding hydrides $\{[C_4H_2O(CH_2C_5H_4)_2\text{-}2,5]Ln(\mu\text{-}H)\}_2$ (**8**; Ln is Y, Nd, Sm, Yb) using NaH, and these were applied as catalysts in the reduction of 1-octene (low activity) and in the dechlorination of benzyl chloride (high activity). The catalytic activities were compared to those of other complexes of ring-linked dicyclopentadienyl ligands [15].

In addition to the bridging ether function, bridging nitrogen donors have also been used. Complexes $\{[MeN(CH_2CH_2C_5H_4)_2]Ln(\mu\text{-}Cl)\}_2$ (**9**; Ln is Y, Nd, Sm, Yb) [16] were synthesized using a procedure similar to that for complexes **1**, and evidence for intramolecular coordination of the amino functionality to the lanthanide metals was obtained from NMR and IR data. In contrast to the monomeric structures of complexes **1**, these complexes were found to be dimeric chloride-bridged species (mass-spectral data). This is in accord with the softer character of the amino donor in complexes **9** as compared with the oxygen donor in complexes **1**.

Similarly, complexes $\{[C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]Ln(\mu\text{-}Cl)\}_2$ (**10**; Ln is Y, Pr, Nd, Sm, Dy, Er, Yb, Lu) [17], containing a bridging pyridine (**Ic**) are also dimeric (mass-spectral data). Evidence for intramolecular coordination of the pyridine functionality in these complexes was again obtained from XPS measurements. Preliminary experiments showed complexes **8** to be active catalysts in the reduction of 1-hexene by

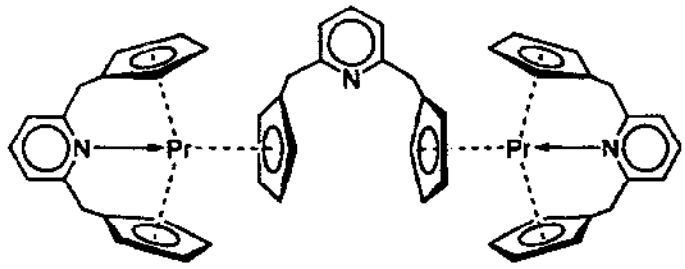
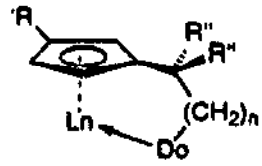



Fig. 1. Schematic representation of the proposed structure of complex **11**.

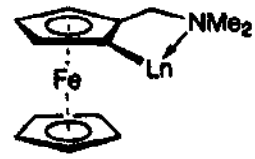
$LiAlH_4$ Reaction of three equivalents of the starting $[C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]Na_2$ with two equivalents of $PrCl_3(THF)_x$ gave rise to the formation of $[C_5H_3N(CH_2C_5H_4)_2\text{-}2,6]_3Pr_2$ (**11**) which was proposed to contain the third ligand in a bridging fashion: $Pr(\eta^5\text{-}C_5H_4CH_2\text{-}2\text{-}(C_5H_3N)\text{-}6\text{-}CH_2C_5H_4\text{-}\eta^5)Pr$, see Fig. 1.

**Type II**
substituted cyclopentadienyl ligands




n = 0: R' = H, $SiMe_3$; R'' = Me;
Do = 2-pyridyl.
n = 1: R' = R'' = H;
Do = OMe, $NMe_2$.
R' = H, $SiMe_3$; R'' = Me;
Do = 2-pyridyl.

**Type III**
substituted ferrocenyl ligands




### 2.2. *Complexes of donor-substituted cyclopentadienyl ligands*

Both Ln(III) and Ln(II) complexes of type **II** ligands have been synthesized using oxygen and nitrogen donor substituents. Complexes $[(MeOCH_2CH_2C_5H_4)_2Ln(\mu\text{-}Cl)]_2$ (**12**; Ln is La, Pr, Nd) [18] and $(Me_2NCH_2CH_2C_5H_4)_2LnCl$ (**13**; Ln is Nd [19], Lu [20]) were synthesized by reaction of $LnCl_3$ with two equivalents of $(DoCH_2CH_2C_5H_4)Na$ (Do is OMe, $NMe_2$) at room temperature in THF, and of both types of complexes X-ray structures have been reported. In the dimeric, chloride-bridged solid-state structure of $[(MeOCH_2CH_2C_5H_4)_2LaCl]_2$ [18] the ether substituents coordinate to the lanthanum metal to which the cyclopentadienyl ligand is $\eta^5$-bonded, leading to formally ten-coordinate lanthanum centers. $^1H$ NMR measurements showed that also in solution the ether functions are coordinating to the metal center.

When the chloride ion in complexes **12** is replaced by the larger iodine, the complexes are monomeric: $(MeOCH_2CH_2C_5H_4)_2LnI$ (**14**; Ln is Y, La [21], Yb [22]). Intramolecular coordination of the methoxy substituents in complexes **14** was observed by IR and NMR spectroscopy (Ln is Y, La) and the monomeric structure was suggested by mass spectroscopy (Ln is Y, La) and firmly established by X-ray

structure analysis (Ln is Y, La, Yb). The structures of all three complexes show both ether substituents to coordinate to the metal centers, resulting in formal nine-coordination. Replacement of methoxy by sterically more demanding dimethylamino substituents as in complexes **13** also prevents dimerization of the resulting complexes, as shown by the monomeric solid-state structure of $(Me_2NCH_2CH_2C_5H_4)_2NdCl$ [19]. In this complex, coordination of both amino functionalities to neodymium also leads to formal nine-coordination.

Reaction of $[(MeOCH_2CH_2C_5H_4)_2LnCl]_2$ with $NaBH_4$ at room temperature in THF leads to the formation of $(MeOCH_2CH_2C_5H_4)_2LnBH_4$ (**15**; Ln is La, Pr, Nd, Sm, Gd) [23]. According to both MS data and the solid-state structures of the complexes with Ln as Pr, Nd, the larger bulkiness of $BH_4^-$ compared to $Cl^-$ (in complexes **12**) makes these complexes monomeric. Reaction of $[(MeOCH_2CH_2C_5H_4)_2LnCl]_2$ with NaH in THF at room temperature affords the hydride complexes $[(MeOCH_2CH_2C_5H_4)_2Ln(\mu\text{-}H)]_2$ (**16**; Ln is Y, La, Pr, Ho) [24], which were reported to be much more soluble in THF than their unsubstituted $C_5H_5$ analogs, but insoluble in aliphatic solvents at room temperature. Their mass spectra and the X-ray structure of the Y-complex showed that these complexes are dimeric in structure. IR measurements showed two separate C–O–C stretching vibrations, which is in accord with the X-ray structure of $[(MeOCH_2CH_2C_5H_4)_2YH]_2$ that shows the ether functionality of one of the two cyclopentadienyl ligands to be coordinated to yttrium in the solid state. As a result of partial hydrolysis during crystallization, complex $[(MeOCH_2CH_2C_5H_4)_2Ho(\mu\text{-}OH)]_2$ (**17**) was obtained, and the X-ray structure of this complex also shows the coordination of only one ether functionality, though the second remains pendant [24].

Up to now complexes $[(MeOCH_2CH_2C_5H_4)_2Ln(THF)]^+[Co(CO)_4]^-$ (**18**; Ln is Sm, Yb) are the only cationic complexes containing donor-substituted cyclopentadienyl ligands reported [25]. These complexes could be synthesized both by metathesis of $[(MeOCH_2CH_2C_5H_4)_2LnI]$ with $K[Co(CO)_4]$ in addition to one-electron oxidation of divalent $(MeOCH_2CH_2C_5H_4)_2Ln(THF)$ (vide infra) with $Co_2(CO)_8$. The X-ray structure of the Yb complex showed **18** to exist as discrete cations and anions, with both ether functionalities coordinating to the ytterbium center in the cation. Together with the additional coordination of one THF solvent molecule, this amounts to a coordination number of nine for the ytterbium ion.

The triscyclopentadienyl complexes $(MeOCH_2CH_2C_5H_4)_3Ln$ (**19**; Ln is Nd [19], La, Pr [26], Sm [22]), synthesized similarly to complexes **12** and **13**, are monomeric, with two of the three available ether functionalities coordinating to the metal centers as shown by both low-temperature $^1H$ NMR spectra and the solid-state structure of the praseodymium [26] and samarium [22] complexes. The third ether function remains pendant. Also in this case, substitution of methoxy for dimethylamino as in complexes $(Me_2NCH_2CH_2C_5H_4)_3Ln$ (**20**; Ln is La, Nd) [19,20] leads to additional steric crowding around the lanthanide centers. In the solid-state structure of $(Me_2NCH_2CH_2C_5H_4)_3Nd$ [20] only one of the three donor substituents coordinates to the neodymium, the other two remaining pendant, as opposed to two of the three in complexes **19**. As a result of the somewhat larger ionic radius of $La^{3+}$ as compared to $Nd^{3+}$, a second amino substituent is able to approach the lanthanum center in

$(Me_2NCH_2CH_2C_5H_4)_3La$, although the La–N distance for this additional interaction in the solid state is very long (3.688(5) Å; cf. 2.898(6) Å for the 'normal' La–N distance in this complex, which itself is long when compared to other La–N interactions) [20]. These effects of steric crowding are even stronger for the smallest lanthanide, lutetium, where the tri-substituted complex is not formed using the reaction conditions for the preparation of complexes **19**, and $(Me_2NCH_2CH_2C_5H_4)_2$ LuCl is obtained instead [20].

In addition to these trivalent lanthanide complexes, divalent lanthanide complexes of type **II** have also been reported for samarium and ytterbium. These complexes were prepared by reaction of the sodium or potassium salts of the ligands with $LnI_2$ in THF solution at room temperature. For complexes $(MeOCH_2CH_2C_5H_4)_2Ln$ (Ln is Sm, Yb) (**21**) [27] and $(Me_2NCH_2CH_2C_5Me_4)_2Sm$ (**22**) [28] intramolecular coordination of the donor substituents was established by NMR spectroscopy and also found in the X-ray structures of $(MeOCH_2CH_2C_5H_4)_2Yb{\cdot}THF$ and the calcium analog of **22**. For complexes $[C_5H_4N\text{-}2\text{-}(CH_2)_nCMe_2C_5H_3R]_2Yb$ ($n=0$, 1; R is H, $SiMe_3$) (**23**) intramolecular coordination of the 2-pyridyl donor in the solid state was established from X-ray structures (for $n=0$, R is H; for $n=1$, R is $SiMe_3$) [29].

Thus far, only one report has appeared on complexes of type **III**. Complexes containing the monoanionic, ferrocene-based ligand $[(C_5H_5)Fe(C_5H_3CH_2NMe_2)]^-$ (FcN) were synthesized by reacting $LnCl_3$ (Ln is La, Ce, Pr, Nd, Yb) or $Cp_2LnCl$ (Sm, Er, Yb) with the lithium complex (FcN)Li in THF at room temperature [30]. Reaction of $LnCl_3$ with three equivalents of (FcN)Li afforded the heterometallic salt-containing and solvent-containing complexes $(FcN)_3Ln{\cdot}LiCl{\cdot}THF$ (**24**; Ln is Ce, Pr, Nd). Only for ytterbium could the salt-containing and solvent-free tris complex $(FcN)_3Yb$ (**25**) be obtained, while with $LaCl_3$ such a complex was not formed and $(FcN)_2LaCl$ (**26**) was obtained instead. Reaction of $Cp_2LnCl$ with one equivalent of (FcN)Li afforded the mixed-ligand complexes $Cp_2Ln(FcN)(THF)_n$ (**27**; Ln is Sm; $n=1$; Ln is Er; $n=0$). In contrast, reaction of $[Cp_2YbCl]_2$ with one equivalent of (FcN)Li gives $CpYb(FcN)_2$ (**28**) as the sole product.

## 3. Alkyl-, aryl- and pyridyl-based ligands (Table 2)

### 3.1. Complexes of donor-substituted aryl ligands

Among the first ligands in organolanthanide chemistry containing donor substituents were those that contained a Ln–C $\sigma$-bond and were derived from alkyl-, aryl- and 2-pyridyl ligands.

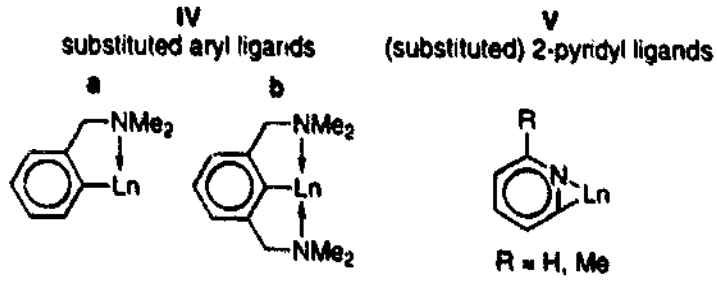


Table 2
Lanthanide complexes of alkyl-, aryl- and pyridyl-based ligands containing intramolecularly coordinating substituents

| | Complex | Lanthanide metals[a] | Ln–Do bond lengths (Å) | Ligand type | Ref. |
|---|---|---|---|---|---|
| 29 | $(C_5H_5)_2Ln[C_6H_4(CH_2NMe_2)\text{-}2]$ | Sc, Y | Y–N: 2.43(2), 2.54(2)[b] | IV | [31, 32] |
| 30 | $(C_8H_8)Ln[C_6H_4(CH_2NMe_2)\text{-}2]\cdot(THF)$ | Er, Lu | Lu–N: 2.479(6) | IV | [33, 34] |
| 31 | $Ln[C_6H_4(CH_2NMe_2)\text{-}2]_3$ | Er, Yb, Lu | Lu–N: 2.588(5), 2.468(6), 2.478(5) | IV | [34, 36] |
| 32 | $(C_5Me_5)Ln[C_6H_4(CH_2NMe_2)\text{-}2]_2$ | Y | Y–N: 2.568(5), 2.506(6) | IV | [37, 38] |
| 33 | $Cp^*Ln[C_6H_4\text{-}2\text{-}CH_2NMe(\mu\text{-}CH_2)][\mu\text{-}C_6H_4\text{-}2\text{-}CH_2NMe(\mu\text{-}CH_2)]LnCp^*\cdot(THF)$[c] | Y | Y–N: 2.405(6), 2.403(6) | — | [38] |
| 34 | $\{LnCl_2[C_6H_3(CH_2NMe_2)_2\text{-}2,6](\mu\text{-}Cl)[\mu\text{-}Li(THF)_2]\}_2$ | Y, Lu | Lu–N: 2.623(5) | IV | [39] |
| 35 | $Ln(\mu\text{-}Cl)[C_6H_3(CH_2NMe_2)_2\text{-}2,6](CH_2SiMe_3)$ | Lu | Lu–N: 2.60(2), 2.541(19) | IV | [39] |
| 36 | $Ln[C_6H_3(CH_2NMe_2)_2\text{-}2,6](CH_2SiMe_3)_2$ | Lu | — | IV | [39] |
| 37 | $(C_5Me_5)_2Ln[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$ | La | La–N: 2.788(3), 2.755(3) | IV | [40] |
| 38 | $(C_5Me_5)_2Ln(C_5H_4N)$[d] | Sc, Y, Lu | Sc–N: 2.14[e] | V | [41–44] |
| 39 | $[(C_5Me_5)_2Ln][\mu\text{-}\eta^2\text{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2]$ | Y | Y–N: 2.348(9), 2.344(9)<br>Y–O: 2.356(8), 2.353(8) | — | [44] |
| 40 | $Li_3[Ln(CH_2CH_2CH_2NMe_2)_3Cl_3](THF)_n$ | La ($n=2$), Pr ($n=0.5$), Er ($n=0$) | — | VIb | [45] |
| 41 | $Li_3[Ln(CH_2CH_2CH_2NMe_2)_6]$ | Ce | — | VIb | |
| 42 | $(C_5H_5)Ln(CH_2CH(R)CH_2NMe_2)Cl(THF)_2$ | Lu (R = H, Me) | Lu–N: 2.637(8) [R = Me] | VIb | [46] |
| 43 | $(C_5H_5)_2Ln(CH_2CH(R)CH_2NMe_2)$ | Lu | Lu–N: 2.37(1) | VIb | [47] |
| 44 | $(C_5H_5)Ln[CH_2CH_2CH_2As(R')_2]_2$ | Lu (R' = Me, $^t$Bu) | — | VIb | [46] |
| 45 | $(C_5H_5)_2Ln(CH_2)PMe_2$ | Lu | — | VIc | [48] |

[a] Underlining indicates that a crystal structure is available. [b] Two crystallographically inequivalent molecules. [c] $Cp^* = C_5Me_5$. [d] Insertion products of this complex have not been included in this table (see text for reference). [e] Estimate, owing to disorder.

All complexes of type **IV** reported thus far have been synthesized by reaction of a lanthanide chloride species with the aryl lithium complex $Li[C_6H_4(CH_2NMe_2)\text{-}2]$ in THF and the earliest report dates back to 1978 [31]. The mono(aryl) complexes $Cp_2Ln[C_6H_4(CH_2NMe_2)\text{-}2]$ (**29**; Ln is Sc [31], Y [32]) (synthesized from $Cp_2LnCl$) are monomeric, very air- and moisture-sensitive, and soluble in both aromatic and ethereal solvents. The solid-state structure of the yttrium complex contains two crystallographically independent molecules in the asymmetric unit and shows the amino substituent to coordinate to the metal center, resulting in a coordination number of seven [32]. In the mono(aryl) complexes $(\eta^8\text{-}C_8H_8)Ln[C_6H_4(CH_2NMe_2)\text{-}2](THF)$ (**30**; Ln is Er, Lu (X-ray)) the amino substituent also coordinates to the lanthanide center, leading to a monomeric complex with coordination number eight [33,34]. These complexes are soluble in THF, but only slightly in aromatic solvents. The lutetium complex $(\eta^8\text{-}C_8H_8)Lu[C_6H_4(CH_2NMe_2)\text{-}2](THF)$ was tested for hydrogenolysis with molecular hydrogen, reaction with CO, and insertion of simple olefins as well as for the reaction with internal alkynes like 1-(trimethylsilyl)propyne [34]. However, it only showed reactivity similar to that of $Cp_2LnR$ (R is alkyl) in its metallation of terminal alkynes like 3,3-dimethyl-1-butyne, with formation of $(\eta^8\text{-}C_8H_8)Lu(C{\equiv}C^tBu)$ [35]. In the reaction with CO, an unidentifiable mixture of products was observed. The observed (lack of) reactivity was attributed to steric saturation of the complex.

The homoleptic complexes $Ln[C_6H_4(CH_2NMe_2)\text{-}2]_3$ (**31**; Ln is Er, Yb, Lu) are also monomeric, soluble in aromatic and ethereal solvents, and slightly soluble in aliphatic solvents [34,36]. The X-ray structure of the lutetium complex shows all amino substituents to be coordinated to lutetium, leading to a coordination number of only six for lutetium in this complex [36]. The reactivity of the lutetium complex $Lu[C_6H_4(CH_2NMe_2)\text{-}2]_3$ resembles that of $(\eta^8\text{-}C_8H_8)Lu[C_6H_4(CH_2NMe_2)\text{-}2](THF)$ (vide supra) with the addition that in the reaction with 3,3-dimethyl-1-butyne the insertion product 2-[*o*-(dimethylamino)methyl]phenyl-3,3-dimethylbutenyl is isolated in addition to the expected *N*,*N*-dimethylbenzylamine [34,36].

Another route to mixed cyclopentadienyl–aryl complexes is the reaction of $Y[C_6H_4(CH_2NMe_2)\text{-}2]_3$ with $C_5Me_5H$ (Cp*H) to give $Cp^*Y[C_6H_4(CH_2NMe_2)\text{-}2]_2$ (**32**) and *N*,*N*-dimethylbenzylamine [37,38]. The solid-state structure of this 14-electron complex shows it to be monomeric, with both amino substituents coordinating to yttrium [38]. However, the two Y–N dative bonds differ substantially (2.568(5) and 2.506(6) Å) and further inspection of the molecular structure shows close Y···H (3.00(6) and 3.13(9) Å) and Y···C (3.202(8) Å) contacts with one of the aminomethyl groups, providing evidence for Y·C–N and Y·C–H agostic interactions. Probably as a result of these interactions, thermolysis of **26** leads to C–H activation in one of the aminomethyl groups, giving $Cp^*Y[C_6H_4\text{-}2\text{-}CH_2NMe(CH_2\text{-}\mu)][\mu\text{-}C_6H_4CH_2NMe(CH_2\text{-}\mu)\text{-}2]YCp^*(THF)$ (**33**) exclusively (see Fig. 2) [38].

The dimeric 'ate'-complexes $\{LuCl_2[C_6H_3(CH_2NMe_2)_2\text{-}2,6](\mu\text{-}Cl)[\mu\text{-}Li(THF)_2]\}_2$ (**34**; Ln is Y, Lu), synthesized by reaction of $LnCl_3$ with $LiC_6H_3(CH_2NMe_2)_2\text{-}2,6$ in THF at room temperature, appear to be excellent precursors for the synthesis of reactive lanthanide dialkyl complexes [39]. Intramolecular coordination of both amino substituents to the metal center was indicated by $^1H$

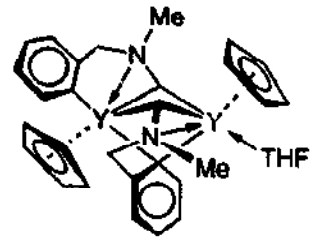
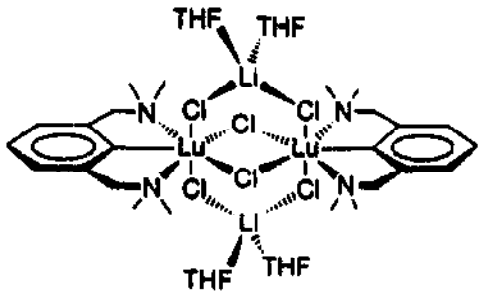


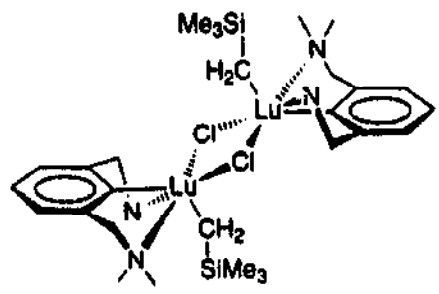

Fig. 2. Schematic representation of complex 33.

NMR and observed in the solid-state structure of the lutetium complex (see Fig. 3). Reaction of **34** (Ln is Lu) with one equivalent of $LiCH_2SiMe_3$ in THF at −78°C afforded dimeric $Lu(\mu\text{-}Cl)[C_6H_3(CH_2NMe_2)_2\text{-}2,6](CH_2SiMe_3)$ (**35**) [39]. As already indicated by $^1H$ NMR, the solid-state structure of this complex shows it to contain the bis(*ortho*)-amino aryl ligand in its pseudo-facial coordination mode (see Fig. 3). Reaction of this complex with an additional equivalent of $LiCH_2SiMe_3$ in THF at −78°C gave rise to the formation of the dialkyl complex $Lu[C_6H_3(CH_2NMe_2)_2\text{-}2,6](CH_2SiMe_3)_2$ (**36**) [39]. Complexes **35** and **36** are unstable in hexane solution and decompose with formation of tetramethylsilane (TMS). This loss of TMS takes place from complex **36** (which is also formed from **35** through a disproportionation reaction) and probably involves formation of an intermediate unstable carbene species $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]Lu{=}CHSiMe_3$. The corresponding yttrium alkyl complexes are even more unstable and could not be isolated.

Although complexes **31** could not be obtained for the early lanthanides, reaction of $(C_5H_5)_3La{\cdot}THF$ with one equivalent of $LiC_6H_3(CH_2NMe_2)_2\text{-}2,6$ in THF at room temperature afforded the monomeric complex $(C_5H_5)_2La[C_6H_3(CH_2NMe_2)_2\text{-}2,6]$ (**37**) [40]. This complex also contains the bis(*ortho*)-amino aryl ligand in its pseudo-facial coordination mode in the solid state (see Fig. 4), leading to two inequivalent cyclopentadienyl ligands and a formal coordination number of nine. In solution, NMR data indicate a symmetric structure, probably as a result of low-energy fluxional processes. Complex **37** is soluble in aromatic solvents and THF, and reacts with proton donors with initial loss of the bis(*ortho*)-amino aryl ligand.




(34)




(35)

Fig. 3. Schematic representations of complexes **34** and **35**, showing the pseudo-facial coordination of the bis(*ortho*)-amino aryl ligand in the latter.

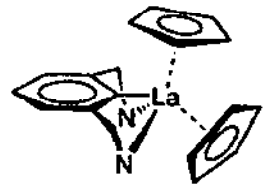



Fig. 4. Schematic representation of complex 37.

### 3.2. Complexes of pyridyl ligands

Complexes of type V can be obtained through C–H activation of pyridine by $(\eta^5\text{-}C_5Me_5)_2LnR$ (for Ln is Lu, R is H, Me [41]; for Ln is Sc, R is H, Me, $C_6H_5$, $CH_2C_6H_5$ [42]; and for Ln is Y, R is H, Me, $CH_2(SiMe_3)_2$ [43,44]). This C–H activation is thought to be an intramolecular process, taking place after initial coordination of pyridine to form $(\eta^5\text{-}C_5Me_5)_2LnR$(pyridine) [41–43]. From the X-ray structure of $(\eta^5\text{-}C_5Me_5)_2Sc(C_5H_4N)$ (**38**) [41], which contains a disordered pyridyl group with estimated Sc–C and Sc–N bond lengths of 2.20 and 2.14 Å, respectively, it appears that a description in terms of an $\eta^2$-C,N interaction is more realistic than intramolecular coordination of the pyridine nitrogen. The reactivity of $(\eta^5\text{-}C_5Me_5)_2Y(C_5H_4N)$ (**38**) was examined in detail [44], and the complex was found to decompose at elevated temperatures with formation of 2,2'-bipyridine through C–C coupling. Mono-insertion products were found in the reaction of **38** with ethylene, propylene and 2-pentyne, leading to lanthanide alkyl complexes with intramolecular coordination (type VI). With terminal alkynes, transmetallation to give the acetylides $(\eta^5\text{-}C_5Me_5)_2Y(C{\equiv}CR)$ (cf. complexes **30** and **31**) was the dominant reaction. Interestingly, reaction of **35** with CO resulted in the formation of the enolate complex $[(\eta^5\text{-}C_5Me_5)_2Y][\mu\text{-}\eta^2{:}\eta^2\text{-}OC(2\text{-}NC_5H_4)_2]$ (**39**) depicted in Fig. 5, which was crystallographically characterized [44].

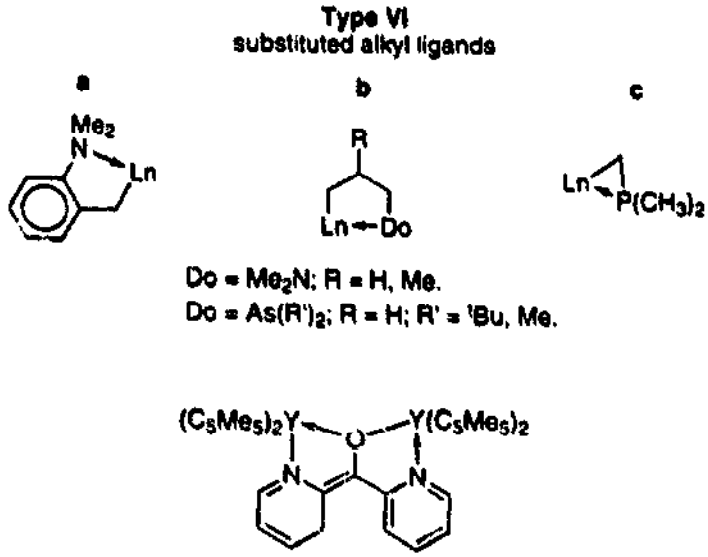



Fig. 5. Schematic representation of complex 39.

### 3.3. Complexes of donor-substituted alkyl ligands

In addition to the complexes of type **VI** obtained by insertion of alkenes or alkynes in the Y–C bond of $(\eta^5\text{-}C_5Me_5)_2Y(C_5H_4N)$ (vide supra), some alkyl ligands containing amino, arseno or phosphino donor groups have been applied in lanthanide chemistry. The 'ate'-complexes $Li_3[Ln(CH_2CH_2CH_2NMe_2)_3Cl_3](THF)_x$ (**40**; Ln is La ($x=2$), Pr ($x=0.5$), Er ($x=0$)) were prepared by reaction of three equivalents of the lithium alkyl with $LnCl_3$ in THF at room temperature [45]. The use of six equivalents of lithium alkyl does not lead to complexes $Li_3[LnR_6]$ (**41**) for Ln is La, Pr, Er, but for Ln is Ce a complex with this stoichiometry is indeed formed. The La and Pr complexes were reported to be insoluble in THF after their isolation from this solvent. The cyclopentadienyl lanthanide alkyl complexes $(C_5H_5)Lu(CH_2CH(R)CH_2NMe_2)Cl(THF)_2$ (**42**; R is H, Me) were prepared by metathesis of $(C_5H_5)LuCl_2(THF)_3$ with one equivalent of the appropriate lithium alkyl in THF [46]. The X-ray structure of complex **42** with R is Me shows the amino substituent to coordinate to lutetium, resulting in a seven-coordinate metal center. The related complexes $(C_5H_5)_2Lu(CH_2CH(R)CH_2NMe_2)$ (**43**; R is H, Me) were prepared by a one-pot synthesis in THF from $LuCl_3$, NaCp and $LiCH_2CH(R)CH_2NMe_2$ in a molar ratio 1:2:1 [47]. The intramolecular coordination of the amino substituent in **43** for R is H was established from a crystal structure determination. Interestingly, the one-pot procedure takes a different course in the presence of $CO_2$ with the formation of the yttrium carboxylate $(C_5H_5)_2Y(\eta^2\text{-}O_2CCH_2CH_2CH_2NMe_2)$. In this complex the bidentate bonding of the carboxylate moiety results in the amino functionality remaining pendant, as shown by the X-ray structure of the complex (Y–N: 4.99 Å) [47].

The only known complexes using a soft arseno donor substituent, $(C_5H_5)Lu[CH_2CH_2CH_2As(R')_2]_2$ (**44**; R' is Me, $^t$Bu), were synthesized by reaction of $CpLu(OSO_2CF_3)_2(THF)_n$ with two equivalents of $ClMg(CH_2)_3As(R')_2$ in THF [46]. However, there is no direct evidence for the intramolecular coordination of the arseno substituents to lutetium, which was postulated by analogy to $(\eta^5\text{-}C_5Me_5)Y[C_6H_4(CH_2NMe_2)\text{-}2]_2$ (**32**).

The first reported phosphine-stabilized lanthanide complex, $(C_5H_5)_2Lu(CH_2)PMe_2$ (**45**), was synthesized by reaction of $(C_5H_5)_2LuCl(THF)$ with $Li(CH_2)PMe_2$ in THF at $-30$°C [48]. Intramolecular coordination of the phosphine donor to lutetium, with formation of a three-membered ring, was postulated on the basis of $^1H$ and $^{13}C$ NMR data, although formation of a six-membered ring as a result of dimerization could not be excluded. Complex **45** was reported to be toluene soluble.

## 4. Alkoxide-, phenolate-, thiolate- and siloxide-based ligands (Table 3)

### 4.1. Complexes of monoanionic, bi- and tridentate ligand systems

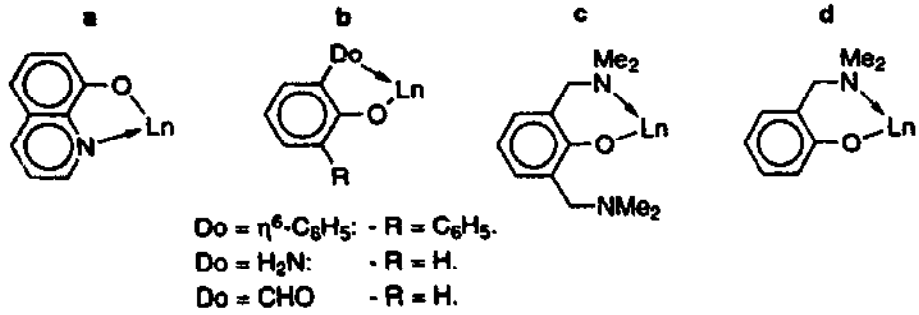
As a result of the interest in the possible use of lanthanide chelate complexes in optical maser (laser) devices in the early 1960s [49], a number of lanthanide com-

| | Complex | Lanthanide metals[a] | Ln–Do bond lengths (Å) | Ligand type | Ref. |
|---|---|---|---|---|---|
| 47 | $[2\text{-}(CHO)C_6H_4O]_3Ln$ | La, Ce, Pr, Nd, Sm, Eu | — | VIIb | [50] |
| 48 | $[2\text{-}(CHO)C_6H_4O]_3Ln\cdot(L)_n$ | La, Pr, Nd, Sm, Eu, Tb[b] | — | VIIb | [51] |
| 49 | $\{[2\text{-}(CHO)C_6H_4O]_4Ln\}M$ | Y (M = Li, Na) | — | VIIb | [52] |
| 50 | $(C_5H_5)_2Ln(8\text{-}OC_9H_6N)$ | Nd, Yb | — | VIIa | [54] |
| 51 | $(C_5H_5)Ln(8\text{-}OC_9H_6N)_2$ | Nd, Yb | — | VIIa | [54] |
| 52 | $(C_5H_5)_2Ln(OC_6H_4NH_2\text{-}2)$ | Nd, Yb | — | VIIb | [54] |
| 53 | $(C_5H_5)Ln(OC_6H_4NH_2\text{-}2)_2$ | Nd, Yb | — | VIIb | [54] |
| 54 | $Ln(OC_6H_3Ph\text{-}2,6)_3$ | Nd, Er, Yb, Lu | Yb–C: 2.978(6)[c] | VIIb | [55] |
| 55 | $\{ClLn[OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4]Na\}$ | Y, Lu | Lu–O: 2.143(3), 2.150(3), 2.174(3)<br>Lu–N: 2.605(4), 2.649(4), 2.656(4) | VIIc | [56,57] |
| 56 | $ClLn[OC_6H_4(CH_2NMe_2)\text{-}2]_3Ln[OC_6H_4(CH_2NMe_2)\text{-}2]_3Na$ | Y | Y–O: 2.236(7), 2.255(6), 2.256(6)<br>Y–N: 2.528(7), 2.564(7), 2.576(9) | VIIc | [57] |
| 57 | $Ln[OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4]_3[OC_6H_2(CH_2NMe_2)\text{-}2(CH_2N(H)Me_2)\text{-}6\text{-}Me\text{-}4$ | Y, La | — | VIIc | [58] |
| 58 | $Ln[OC_6H_4(CH_2NMe_2)\text{-}2]_3[OC_6H_4(CH_2N(H)Me_2)\text{-}2]$ | Y, La | La–O: 2.319(4), 2.330(3), 2.334(4), 2.404(2)<br>La–N: 2.744(5), 2.747(5), 2.783(4) | VIIc | [58] |
| 59 | $Ln[OC(^tBu)_2CH_2PMe_2]_3$ | Y, Nd | Y–P: 3.045(2)[c]; Nd–P: 3.154(1)[d] | VIIIa | [61] |
| 60 | $Ln[OC(R^1)(R^2)CH_2OEt]_3$[e] | Nd | — | VIIIa | [62] |
| 61 | $Ln[OC(R^1)(R^2)CH_2NEt_2]_3$[e] | Nd | — | VIIIa | [62] |
| 62 | $Ln[OC(^tBu)_2CH_2NEt_2]_3$ | Y | — | VIIIa | [62] |
| 63 | $Ln[OC_6H_4Me\text{-}1\text{-}OMe\text{-}2]_3$ | Nd | — | VIIIb | [62] |
| 64 | $[Ln[OCH_2CH_2OMe)_3]_{10}$ | Y | Y–O: 2.52(2)[c] | VIIIa | [63] |
| 65 | $Ln_3[OCH_2CH_2OMe)_5(acac)_4$[f] | Y | Y–O: 2.52(2)–2.57(2) | VIIIa | [65] |
| 66 | $(thd)_4Cu_3Ln(OCH_2CH_2OMe)_5$[g] | Y | Y–O: 2.530(11) | VIIIa | [66] |
| 67 | $[(hfd)_2CuLn(OCH_2CH_2OMe)_3]_2$[h] | Y | Y–O: 2.526(11) | VIIIa | [66] |
| 68 | $(hfd)_2(thd)_2Cu_2Ln(OCH_2CH_2OMe)_3$[g,h] | Y | Y–O: 2.789(5), 2.687(6) | VIIIa | [66] |
| 69 | $LnCu_2(bdmap)_3(O_2CCF_3)_4$[i] | La, Nd | La–N: 2.85(2) | VIIIc | [67] |
| 70 | $[Cu_3(bdmap)_3(O_2CCF_3)_2]_2[Ln_2(bdmap)_2(O_2CCF_3)_6]$ | Y | Y–N: 2.72(5), 2.64(4) | VIIIc | [67] |
| 71 | $[C_5H_5)Ln(iba)]_2$ | Yb | Yb–O: 2.382(6), 2.394(7) | VIIId | [68] |
| 72 | $Ln\{OSi(^tBu)_{3-n}[(CH_2)_3NMe_2]_n\}_3$ | Y ($n$ = 1, 2), Ce ($n$ = 1) | Y–N: 2.629(8), 2.595(9) [$n$ = 1] | IXa | [69] |
| 73 | $Ln[OSi(^tBu)_2(CH_2)_3NMe_2]_3$ | Y | — | IXa | [69] |
| 74 | $Ln[OSi^tBu(C_6H_4CH_2NMe_2\text{-}2)_2][N(SiMe_3)_2]_2$ | Y | Y–N: 2.611(9) | IXb | [70] |
| 75 | $Ln[OSi^tBu(C_6H_4CH_2NMe_2\text{-}2)_2][OC_6H_3{}^tBu_2\text{-}2,6]_2$ | Y | — | IXb | [70] |
| 76 | $\{Ln[OSi^tBu(C_6H_4CH_2NMe_2\text{-}2)_2][OC_6H_3{}^tBu_2\text{-}2,6](CH_2SiMe_3)_2\}^-Li^+$ | Y | — | IXb | [70] |
| 77 | $[(C_5H_5)Fe(2\text{-}CH_2NMe_2)C_5H_3S)]_{3-n}LnCl_n$ | Yb ($n$ = 0, 1) | — | X | [71] |

[a] Underlining indicates that a crystal structure is available. [b] $n$ = : L = 1,10-phenanthroline, 2,2-bipyridine; $n$ = 2: L = quinoline, pyridine. [c] Average of Yb–C bond lengths in single $\eta^6$-arene interaction. [d] Average value. [e] $R^1$ = H, $^t$Bu, $^i$Pr; $R^2$ = $^t$Bu, $^i$Pr. [f] acac = acetylacetonate. [g] thd = 2,2,6,6-tetramethyl-3,5-heptanedionate. [h] hfd = 1,1,1,5,5,5-hexafluoroacetylacetonate. [i] Hbdmap = 1,3-bis(dimethylamino)propan-2-ol.

plexes of type **VIIb** using salicylaldehyde (2-(CHO)$C_6H_4OH$; Hsal) were prepared and characterized mainly for their optical properties.

**Type VII**
donor substituted phenolate ligands




Do = $\eta^6$-$C_5H_5$: - R = $C_6H_5$.
Do = $H_2N$: - R = H.
Do = CHO - R = H.

The insoluble complexes $Ln(sal)_3$ (**47**; Ln is La, Ce, Pr, Nd, Sm, Eu) were prepared by reacting $LnCl_3$ with three equivalents of Na(sal) in a water/alcohol mixture [50]. Although intramolecular coordination of the aldehyde carbonyl to the lanthanide metal would be expected on the basis of the absence of additional ligands (elemental analyses were satisfactory), the frequency of the carbonyl stretching vibration appeared to be insensitive to the nature of the lanthanide metal. In addition, complexes $Ln(sal)_3(L)_n$ (**48**; Ln is La, Pr, Nd, Sm, Eu, Tb; for $n=1$, L is 1,10-phenanthroline, 2,2'-bipyridine; for $n=2$, L is quinoline, pyridine) are readily formed in the presence of additional nitrogen ligands [51].

The steric unsaturation in complexes **47** is further illustrated by the isolation of the tetrakis(salicylaldehydato) complexes $M[Y(sal)_4]$ (**49**; M is Li, Na) [52]. In agreement with the synthesis of **47**, $Na[Y(sal)_4]$ was prepared by reaction of $Y(sal)_3$ with another equivalent of Na(sal), using salicylaldehyde itself as solvent; the lithium complex could be synthesized in one step. For complexes **49**, the observation of a single phenolate C–O stretching vibration in the IR spectra is strong evidence that all four ligands coordinate in a bidentate fashion [52]. When the insolubility of complexes **47** in polar solvents like water is taken into account, a polymeric structure for these complexes appears likely.

As the synthesis of well-defined 8-quinolinolate complexes (**VIIa**) of the lanthanides starting from $Ln(NO_3)_3$ in acetic acid failed [53], complexes $(C_5H_5)_2Ln(8\text{-}OC_9H_6N)$ (**50**) and $(C_5H_5)Ln(8\text{-}OC_9H_6N)_2$ (**51**) (Ln is Nd, Yb) were synthesized from $(C_5H_5)_3Ln$ and 8-hydroxyquinoline in THF at room temperature [54]. The same procedure using 2-aminophenol (**VIIb**; Do is $NH_2$), resulted in the formation of complexes $(C_5H_5)_2Ln(OC_6H_4NH_2\text{-}2)$ (**52**) and $(C_5H_5)Ln(OC_6H_4NH_2\text{-}2)_2$ (**53**) (Ln is Nd, Yb) [54]. Both IR and XPS spectral data for complexes **50**–**53** provide proof for intramolecular coordination of the nitrogen functionalities to the lanthanide centers in these complexes. In addition, cryoscopic measurements showed the complexes to exist as monomers in solution. The complexes were reported to disproportionate into the homoleptic complexes at moderately high temperatures (below 300°C) as a result of the high transferability of the cyclopentadienyl ligands. Mass-spectral data showed the ytterbium complexes to be thermally more stable than the

corresponding neodymium complexes. This was attributed to the smaller ionic radius of $Yb^{3+}$ as compared to $Nd^{3+}$, leading to a stronger Ln–ligand bond.

A relatively uncommon form of intramolecular coordination was observed for $Yb(OC_6H_3Ph\text{-}2,6)_3$ (**54**) in the solid state, where one of the *ortho*-phenyl substituents has an $\eta^6$-arene interaction with the ytterbium center (**VIIb**; Do is $\eta^6$-$C_6H_5$), as depicted in Fig. 6 [55]. Identical complexes were also prepared for the lanthanides Nd, Er, and Lu, but no information on the coordination geometry of the ligands could be obtained from IR or NMR data. The $\eta^6$-arene interaction is undoubtedly a result of the electronic unsaturation of the ytterbium ion in the solvent-free tris-phenolate complex. This is illustrated by the fact that the complex is prepared by drying under vacuum of $Yb(OC_6H_3Ph\text{-}2,6)_3(THF)_2$.

The unique heterometallic complexes {ClLn[$OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4]Na} (**55**; Ln is Y, Lu) of type **VII** were obtained by reaction of $LnCl_3$ with three equivalents of $NaOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4 in THF at room temperature [56,57]. The crystal structure of the lutetium complex shows it to consist of the chloride, lutetium and sodium atoms, lying on a pseudo-threefold axis, with the three phenolate ligands bridging the lutetium and sodium atoms (see Fig. 7). The phenolate ligands each coordinate with one amino substituent to lutetium and with the other to sodium, resulting in a complex with screw-type chirality. Complexes **55** are soluble in hexane, aromatic solvents and THF. Low-temperature NMR studies ($^1H$ and $^{13}C$) have shown that the structure in solution closely resembles that in the solid state. The self-assembly of complexes **55** is described in terms of positive cooperativity in

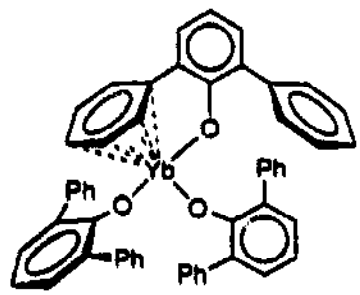



Fig. 6. Schematic representation of complex **54**.

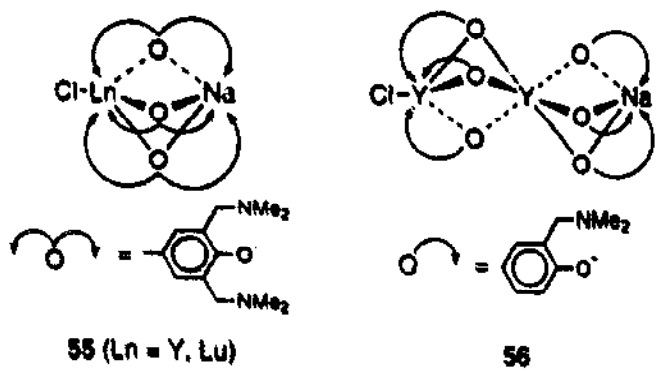
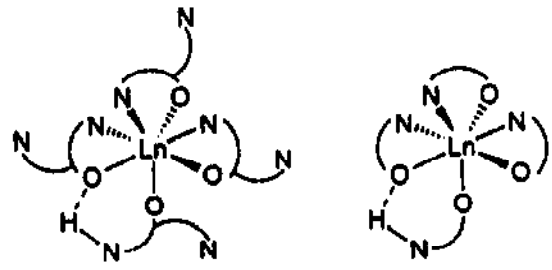



Fig. 7. Schematic representations of the heterometallic complexes **55** and **56**.

binding of the chloride and sodium ions [56,57]: coordination of chloride anion to the unsaturated metal tris-phenolate $Ln[OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4] leads to preorganization of available binding sites in the resulting anion for coordination of sodium cation.

This positive cooperativity is also the driving force for the self-assembly of the (hetero)trimetallic complex $\{ClY[OC_6H_4(CH_2NMe_2)$-2$]_3Y[OC_6H_4(CH_2NMe_2)$-2$]_3Na\}$ (**56**) [57]. This complex was obtained in quantitative yield following the procedure described above for complexes **55**, but using $NaOC_6H_4(CH_2NMe_2)$-2. The solid-state structure of **56** shows it to contain one group of three phenolate ligands bridging the two yttrium atoms, with their amino substituents coordinated to the yttrium bearing the chloride. The second group of three phenolate ligands bridges the other yttrium and the sodium atom, with their amino substituents coordinated to sodium (see Fig. 7). The complex shows structural characteristics that closely resemble complexes **55** and contains two shells of screw-type chirality, which have opposite senses of rotation. Using $^{89}Y$ NMR, an $^{89}Y$–$^{89}Y$ coupling of 0.4 Hz was observed [57]. In combination with $^1H$ and $^{13}C$ NMR data, this showed that the solid-state structure is retained in solution. Complex **56** is soluble in aromatic solvents and THF, but only very slightly soluble in hexane. Complexes **55** and **56** provide new leads for the preparation of heterometallic precursors for the preparation of lanthanide-containing ceramics, as well as a new type of coordination polymer.

In an attempt to avoid the inclusion of salt, observed in complexes **55** and **56**, and possibly obtain complexes with available binding sites, the salt-free lanthanide precursors $Ln[N(SiMe_3)_2]_3$ were used. From the reaction of these precursors with four equivalents of the parent phenols $HOC_6H_2(CH_2NMe_2)_2$-2,6-Me-4 and $HOC_6H_4(CH_2NMe_2)$-2, complexes $Ln[OC_6H_2(CH_2NMe_2)_2$-2,6-Me-4$]_3[OC_6H_2(CH_2NMe_2)$-2$(CH_2N(H)Me_2)$-6-Me-4 (**57**; Ln is Y, La) and $Ln[OC_6H_4(CH_2NMe_2)$-2$]_3[OC_6H_4(CH_2N(H)Me_2)$-2] (**58**; Ln is Y, La), respectively, were obtained [58]. The X-ray structure of complex **58** (Ln is La) shows it to contain three bidentate O,N-bonded phenolate ligands and one neutral phenol. This neutral phenol is bonded in its zwitterionic form: attached to the metal center through its phenolate oxygen and with its protonated amino substituent involved in a strong N–H·O hydrogen bridge (see Fig. 8). The strong similarities between the NMR data

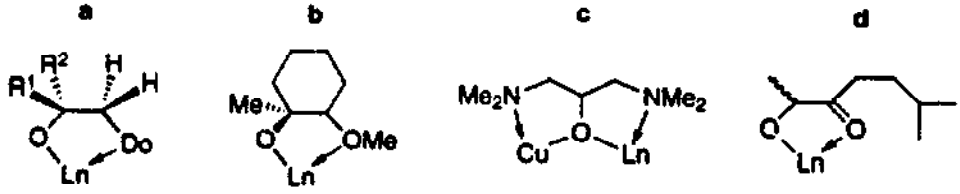



**57** (Ln = Y, La) **58** (Ln = Y, La)

Fig. 8. Schematic representations of complexes **57** and **58**, showing the N–H···O bridges.

for complexes **57** and **58** indicate that the complexes are isostructural, with the additional amino substituents in the former remaining pendant. Both complexes **57** and **58** are soluble in aromatic and ethereal solvents, while the latter are also reasonably soluble in hexane.

**Type VIII**
donor substituted alkoxide ligands




Do = $Me_2P$: - $R^1 = R^2 = {}^tBu$.
Do = MeO: - $R^1 = R^2 = H$.
Do = $OC_2H_5$: - $R^1 = H$; $R^2 = {}^tBu$.
- $R^1 = R^2 = {}^tBu$.
- $R^1 = R^2 = CH(CH_3)_2$.
Do = $NEt_2$: - $R^1 = H$; $R^2 = {}^tBu$.

bdmap

iba

The growing interest in complexes of donor-substituted alkoxide ligands (type **VIII**) is the result of the search for monomeric, organic-solvent-soluble alkoxides of the lanthanides as precursors for lanthanide-oxide-containing ceramics via the sol–gel [59] or MOCVD process [60]. The first monomeric, homoleptic lanthanide alkoxides of this type were $Ln[OC({}^tBu)_2CH_2PMe_2]_3$ (**59**; Ln is Y, Nd), which were synthesized from $LnCl_3$ and the lithium alkoxides [61]. These complexes were also the first lanthanide tertiary phosphine complexes. The identical solid-state structures of the two compounds show the tertiary phosphines to be coordinated to the lanthanide centers, although the Ln–P distances are somewhat long at an average of 3.045(2) and 3.154(2) Å for the yttrium and neodymium complexes, respectively. These long bond distances may be the result of a relatively weak interaction and/or the low affinity of the hard metal for the soft donor [61]. In any case, the presence of the two *tert*-butyl substituents on each alkoxide ligand may well be responsible for the actual steric saturation of the metal center and thus the monomeric structure of the complexes.

Other examples of monomeric complexes of type **VIII** also contain bulky substituents on the carbon $\alpha$ to the anionic oxygen donor. Complexes $Nd[OC(R^1)(R^2)CH_2Do]_3$ (Do is OEt (**60**), $NEt_2$ (**61**); $R^1$ is H, $^tBu$, $CH(CH_3)_2$; $R^2$ is $^tBu$, $CH(CH_3)_2$) and $Y[OC({}^tBu)_2CH_2NEt_2]_3$ (**62**) were all synthesized by reaction of $Ln[N(SiMe_3)_2]_3$ with the appropriate alcohol at room temperature in hexane [62]. These complexes are soluble in aliphatic solvents, and show the highest volatilities achieved so far for lanthanide alkoxide complexes: sublimation temperatures range from 95 to 175°C at $10^{-3}$ mbar. Replacement of the sterically flexible $C(R^1)(R^2)CH_2$ bridge between the anionic and neutral binding sites in these complexes by a 1,2-cyclohexane bridge (**63**; **VIIIb**) was reported to lead to a reduction in volatility [62].

The absence of bulky substituents on the alkoxide ligand, even in the presence of

a hard donor substituent like oxygen, as in complexes of the simple alkoxide ligand $(OCH_2CH_2OMe)^-$ invariably leads to oligomeric structures. For example, the solid-state structure of $[Y(\mu_2,\eta^2\text{-}OCH_2CH_2OMe)_2(\mu_1,\eta^1\text{-}OCH_2CH_2OMe)]_{10}$ (**64**) is a cyclic decamer [63]. This complex, which could be prepared both by direct attack of the alcohol on metallic Y turnings or by alcoholysis of $Y_5O(O^iPr)_{13}$ [64], was found to be highly soluble, but air-sensitive and non-volatile. An oligomeric structure is also present in the mixed-ligand complex $Y_3(\mu_3,\ \eta^2\text{-}OCH_2CH_2OMe)_2(\mu_2,\ \eta^2\text{-}OCH_2CH_2OMe)_2(\mu_2,\ \eta^1\text{-}OCH_2CH_2OMe)\text{-}(acac)_4$ (acac is acetylacetonate) (**65**), which was obtained in an attempt to prepare a pre-ceramic mixed-metal complex by mixing $Cu(acac)_2$ (three equivalents) with **64** [65]. Such mixed-metal complexes could be obtained by mixing **64** with $[(thd)Cu(OCH_2CH_2OMe)]_4$ or $[(hfd)Cu(OCH_2CH_2OMe)]_4$ (thd is 2,2,6,6-tetramethyl-3,5-heptanedionate; hfd is 1,1,1,5,5,5-hexafluoroacetylacetonate) to give complexes $(thd)_4Cu_3Y(OCH_2CH_2OMe)_5$ (**66**) and $[(hfd)_2CuY(OCH_2CH_2OMe)_3]_2$ (**67**), respectively [66]. Complex $(hfd)_2(thd)_2YCu_2(OCH_2CH_2OMe)_3$ (**68**) was obtained when in situ prepared "$[(hfd)_2Y(OCH_2CH_2OMe)]_n$" was mixed with $[(thd)Cu(OCH_2CH_2OMe)]_4$. Complex **65** was reported to be soluble in both aliphatic and aromatic solvents [65]. Complexes **66** and **68** are soluble in polar, aromatic and aliphatic solvents, as well as in the parent alcohol $HOCH_2CH_2OMe$, while complex **67** is only very slightly soluble in THF, $CHCl_3$ and aromatic solvents [66]. The X-ray structures of the heterometallic complexes **66** and **67** show the alkoxide ligand to be present both with the ether substituent pendant and coordinated to copper or yttrium.

Other examples of well-characterized pre-ceramic mixed-metal complexes have been obtained by using 1,3-bis(dimethylamino)propan-2-ol (Hbdmap; **VIIIc**) as a cross-linker. The heterometallic complex $LnCu_2(bdmap)_3(O_2CCF_3)_4$ (**69**; Ln is La, Nd) and $Cu_3(bdmap)_3(O_2CCF_3)_2]_2[Y_2(bdmap)_2(O_2CCF_3)_6$ (**70**) were obtained from pre-ceramic mixtures of $Ln(O_2CCF_3)_3(H_2O)_4$, $Ba(O_2CCF_3)_2$, $Cu_2(O_2CCF_3)_4(H_2O)_2$ and Hbdmap and could also be synthesized independently by reaction of $LnCl_3$, $CuCl_2$, $Ag(O_2CCF_3)$, $Cu(OCH_3)_2$ and Hbdmap in THF [67]. The X-ray structures of complex **69** (Ln is La) and **70** show the bis(amino)alkoxide to bridge two (different) metal atoms, with the amino substituents each coordinating to one of these metal centers (see Fig. 9). The $YBa_2Cu_3O_{7-x}$ powder obtained from

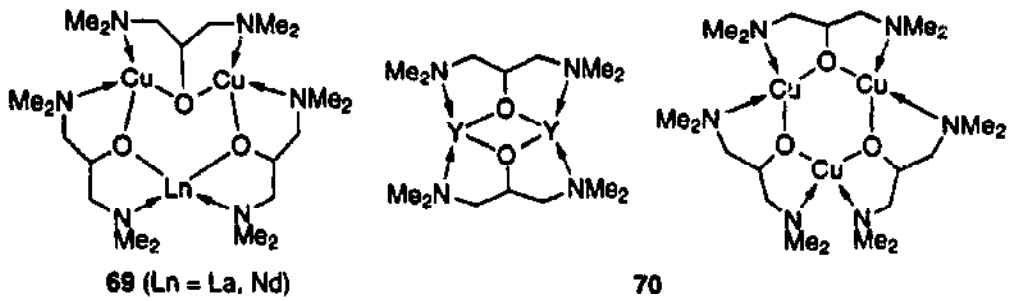
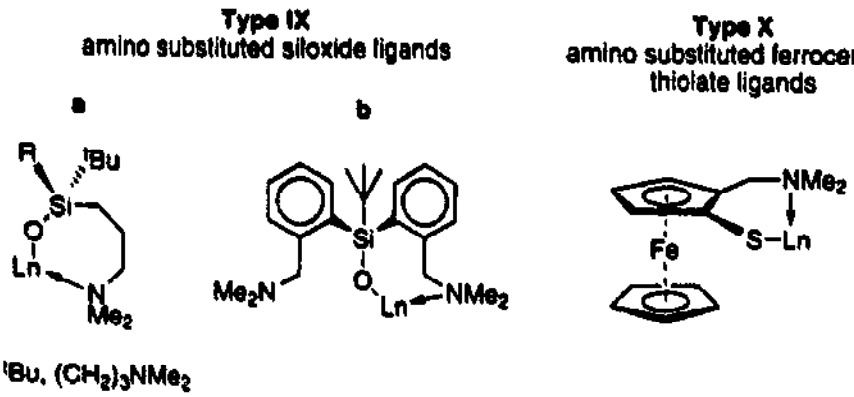



Fig. 9. Schematic representations of complex **69** and the cation (middle) and anion (right) of complex **70**, showing the coordination geometries of the bdmap ligand. Other ligands have been omitted for clarity.

the pre-ceramic mixture (using acetate instead of trifluoroacetate) was reported to have an onset superconducting temperature of 92 K [67].

By reacting optically active (*R*)-(+)-, or (*S*)-(−)-isobutylacetate (iba) with $Cp_3Yb$ in $CH_2Cl_2$ at −40 to −70°C, the dimeric complexes $[Cp_2Yb(iba)]_2$ (**71**) were obtained [68]. IR measurements showed the presence of intramolecular coordination of the carbonyl oxygen to ytterbium, while mass spectra indicated a dimeric, alkoxide-bridged structure. The X-ray structure of the *R* complex shows the isobutylacetate ligands to bridge the two ytterbium ions in a dinuclear arrangement, with the carbonyl oxygens each coordinating to one of the ytterbium ions. The resulting rigid dinuclear complexes **71** were reported to display notable *f-f* circular dichroism.

In the first of only two reports so far on complexes of donor-substituted siloxide complexes, bulky substituents are present on silicon in addition to the amine donor substituent (**IXa**), to effect monomeric structures by analogy to complexes **59–63**. Complexes $Ln\{OSi(^tBu)_{3-n}[(CH_2)_3NMe_2]_n\}_3$ (**72**; for $n=1$, Ln is Y, Ce; for $n=2$, Ln is Y) were synthesized by reaction of $Ln[N(SiMe_3)_2]_3$ with the appropriate silanol (three equivalents) at room temperature in toluene and subsequently recrystallized from toluene/hexane mixtures [69]. The solid-state structure of $Y[OSi(^tBu)_2(CH_2)_3NMe_2]_3$ shows two amino substituents to be coordinated to yttrium, resulting in a coordination number of only five, and the third amino substituent remains pendant. In solution, rapid exchange between coordinated and pendant amino substituents leads to the observation of only one set of signals for the ligands by NMR ($^1H$ and $^{29}Si$). When four equivalents of the silanol are used during the synthesis, the zwitterionic tetrakis(siloxide) complexes $Ln[OSi(^tBu)_2(CH_2)_3NMe_2]_3$ $[OSi(^tBu)_2(CH_2)_3NHMe_2]$ (**73**; Ln is Y, Yb) are obtained, in which the proton counterion is present as an N–H·N bridge between two pendant amino substituents. However, as a result of the steric bulk of the four siloxide ligands, the other two amino substituents are also pendant in the solid-state structure of the ytterbium complex. In solution, an equilibrium was observed between complexes **73** on one hand and the free silanol in combination with the tris(siloxide) complexes **72** on the other hand.

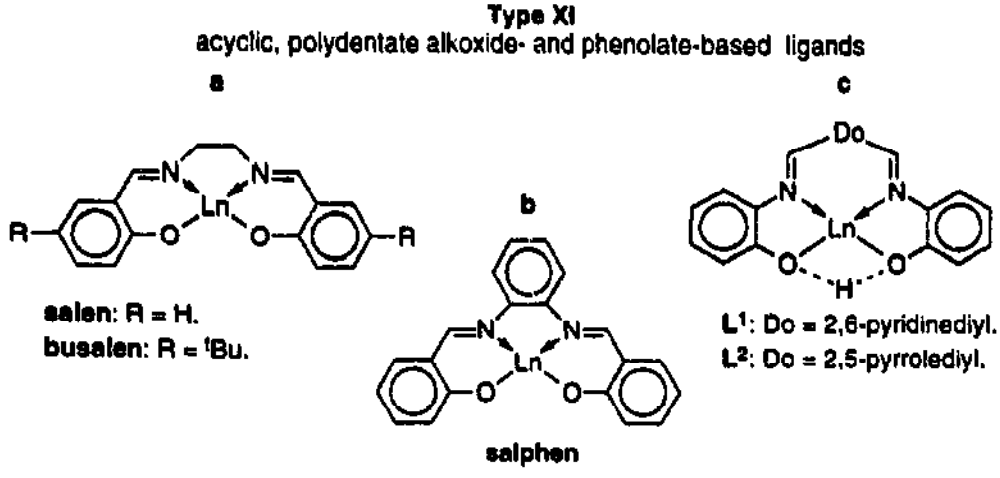



The arylsiloxide complex $Y[OSi^tBu(C_6H_4CH_2NMe_2\text{-}2)_2][N(SiMe_3)_2]_2$ (**74**) was prepared by a procedure similar to that for **72** and **73**, but now using only one equivalent of the silanol at reflux temperature in toluene [70]. The complex shows

complex fluxional behavior in solution as observed by NMR spectroscopy ($^1H$ and $^{89}Y$), but in the temperature range of $-40$ to $+50°C$, coordination of one of the two available amino substituents is observed. This was confirmed by the X-ray structure of the complex, which shows one of the amino substituents to coordinate to yttrium, while the second remains pendant. Together with the two amido ligands, this amounts to a coordination number of only four, which is stabilized by the steric bulk of both the siloxide and amido ligands. Reaction of **74** with two equivalents of $HOC_6H_3{}^tBu_2$-2,6 at reflux temperature in toluene afforded the bis-phenolate $Y[OSi^tBu(C_6H_4CH_2NMe_2\text{-}2)_2][OC_6H_3{}^tBu_2\text{-}2,6]_2$ (**75**), which was prepared as a precursor for yttrium dialkyl complexes [70]. In an attempt to prepare these dialkyl complexes by reacting **75** with two equivalents of neosilyl lithium, loss of only one phenolate ligand led to the complex $\{Y[OSi^tBu(C_6H_4CH_2NMe_2\text{-}2)_2][OC_6H_3{}^tBu_2\text{-}2,6](CH_2SiMe_3)_2\}^-Li^+$ (**76**) [70]. On account of its solubility in toluene and the bulk of the ligands, a monomeric structure was reported to be likely for this complex. However, the presence of two signals in the $^{89}Y$ spectrum of **76** (about 2:1 relative intensity) at $-70°C$ in toluene is indicative of aggregation.

The bimetallic complexes $[(C_5H_5)Fe(2\text{-}(CH_2NMe_2)C_5H_3S)]_{3-n}YbCl_n$ (77; $n=0$, 1) of type X are soluble in aromatic solvents and were synthesized from $YbCl_3$ and the lithium thiolate at room temperature in THF [71]. NMR data indicated that in the tris(ferrocenylthiolate) complex only two amino substituents are coordinated to the metal center, one remaining pendant.

### 4.2. *Complexes of acyclic, polydentate ligand systems (Table 4)*




In addition to the monoanionic, potentially bidentate ligands mentioned thus far in this paragraph, mono-, di- and trianionic polydentate ligands have also been applied in lanthanide chemistry. The lanthanide complexes of bis-salicylaldehyde ethylenediamine (salen, R is H; busalen, R is 'Bu; **XIa**) and bis-salicylaldehyde *o*-phenylenediamine (salphen, **XIb**) have the composition $[Ln_2L_3]\cdot(C_2H_5OH)_n$ (for L is salen (**78**): $n=0$, Ln is La, Pr, Nd, Er, Yb; $n=2$, Ln is Y, Sm, Gd; $n=3$, Ln is Dy; for L is busalen (**79**): $n=0$, Ln is Pr, Nd, Sm, Eu, Gd, Ho; for L is salphen (**80**): $n=$

Table 4
Lanthanide complexes of acyclic, polydentate alkoxide- and phenolate-based ligands

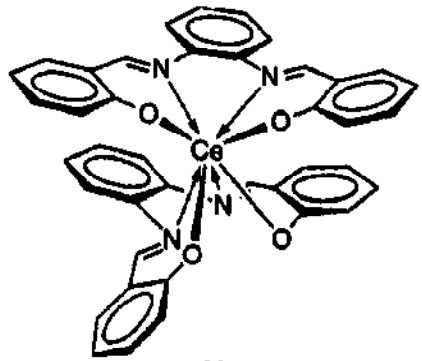
| | Complex | Lanthanide metals[a] | Ln–Do bond lengths (Å) | Ligand type | Ref. |
|---|---|---|---|---|---|
| 78 | $[Ln_2(salen)_3]\cdot(C_2H_5OH)_n$ | La, Pr, Nd, Er, Yb ($n=0$); Y, Sm, Gd ($n=2$); Dy ($n=3$) | — | XIa | [72] |
| 79 | $La_2(busalen)_3$ | Pr, Nd, Sm, Eu, Gd, Ho | — | XIa | [73] |
| 80 | $Ln_2(salphen)_3$ | La, Pr, Nd | — | XIb | [72] |
| 81 | $Ln(salen)_2$ | Ce | — | XIa | [72] |
| 82 | $Ln(busalen)_2$ | Ce | — | XIa | [73] |
| 83 | $Ln(salphen)_2$ | Ce | Ce–N: 2.564(4)–2.645(3) | XIb | [75] |
| 84 | $M[Ln(salphen^1)_2]$ | Y, La, Gd, Yb (M = Li, Na, K, Cs) | — | XIb | [52] |
| 85 | $Ln(HL^1)(NO_3)_2\cdot(H_2O)_n$[b] | Y, La, Ce ($n=2$); Pr, Gd, Dy, Er, Yb ($n=1$) | — | XIc | [76] |
| 86 | $Ln(HL^2)(NO_3)_2\cdot(H_2O)_n$[c] | Pr, Gd, Dy, Er ($n=1$); Sc, Y, La ($n=2$) | — | XIc | [77] |
| 87 | $Ln(HL^2)(NO_3)_3\cdot(H_2O)_2$[c] | Ce | — | XIc | [77] |
| 88 | Ln(trac)[d] | La, Sm, Er, Yb | Yb–N: 2.41(1)–2.46(1)[e] | XId | [79] |
| 89 | Ln(hatren)[f] | La, Sm, Yb | — | XIe | [79] |
| 90 | Ln(datren)[g] | La, Sm, Yb | — | XIe | [79] |
| 91 | $[Ln(L^3)]_2$[h] | Y, La, Pr, Nd, Gd, Dy | Gd–N: 2.813(3), 2.694(3), 2.657(3), 2.615(3) | XIf | [80] |
| 92 | $[Ln(L^4)]_2$[i] | La, Gd | — | XIf | [80] |
| 93 | $[Ln(L^5)]_2$[j] | La, Nd, Gd | — | XIf | [80] |
| 94 | $Ln(L^6)$[k] | Gd | — | XIf | [80] |
| 95 | $Ln(L^7)\cdot(H_2O)_n$[l] | La, Pr, Sm, Gd, Dy, Yb | — | XIg | [82] |
| 96 | $Ln(L^8)(NO_3)_2X$[l] | La, Nd (X = $H_2O$); Pr (X = MeOH) | Pr–N: 2.647(4), 2.661(4), 2.673(4), 2.722(4) | XIh | [83] |
| 97 | $[(R,R)\text{-}L^9]LnI$[l] | Sc, Y, La, Nd, Sm, Tb, Lu | — | XIi | [84] |

[a] Underlining indicates that a crystal structure is available. [b] $L^1$ = 2,6-pyridinediylbis[*N*-(2-oxophenylaldimine)]. [c] $L^2$ = 2,5-pyrrolediylbis[*N*-(2-oxophenylaldimine)]. [d] trac = tris(3-aza-4-methyl-6-oxohept-4-en-1-yl)amine. [e] Two crystallographically inequivalent molecules. [f] hatren = tris((2-oxobenzyl)imino)ethyl)amine. [g] datren = tris((2-oxo-4,5-dimethylbenzyl)imino)ethyl)amine. [h] $L^3$ = tris(((2-oxobenzyl)amino)ethyl)amine. [i] $L^4$ = tris(((2-oxo-5-chlorobenzyl)amino)ethyl)amine. [j] $L^5$ = tris(((2-oxo-5-bromobenzyl)amino)ethyl)amine. [k] $L^6$ = tris(((2-oxo-3-methoxybenzyl)amino)ethyl)amine. [l] For ligand numbering, see figures in text.

0, Ln is La, Pr, Nd), with the exception of cerium(IV) complexes, which have $Ce(L)_2$ stochiometry (L is salen (**81**), busalen (**82**)) [72,73]. Complexes **78–80** were prepared by addition of $Ln(NO_3)_3$ to a solution of the ligand ($H_2$salen, $H_2$busalen or $H_2$salphen) in ethanol [72], methanol [74], acetone [73] or DMF [52] at 55–80°C, followed by the addition of a base (ammonia gas, aqueous ammonia [72], triethylamine [52]). The cerium(IV) complexes **81** and **82** could be prepared by using either $(NH_4)_2Ce^{IV}(NO_3)_6$ or $Ce^{III}(NO_3)_3{\cdot}(H_2O)_6$. The busalen complexes **79** are, as a result of the presence of the *tert*-butyl substituents, soluble in $CHCl_3$. All other complexes are crystalline, melt with decomposition above 260°C (**80**), 280°C (**81**) or 300°C (**78**) and are soluble in dimethylformamide (DMF), but insoluble in common organic solvents. $Ce(salphen)_2$ (**83**) was prepared in a procedure similar to that for **81**, using DMF as the solvent, from which it could also be crystallized [75]. The crystal structure of this complex shows the Ce(IV) center to be sandwiched between the two salphen ligands, with all anionic oxygen and neutral nitrogen donor sites coordinated to the metal center, resulting in formal eight-coordination (see Fig. 10).

Despite several attempts, no crystals suitable for X-ray analysis could be obtained thus far for complexes **78–80**, and, although structures have been proposed on the basis of the composition and spectroscopic data for these complexes and the structure of complex **83** [52,72,73], the matter remains unresolved. Complexes $M[Ln(salphen)_2]$ (**84**; M is Li, Na, K, Cs; Ln is Y, La, Gd, Yb) were prepared by two different procedures, depending on both the lanthanide and alkali metals [52]: (i) addition of $Ln(NO_3)_3{\cdot}(DMSO)_n$ (Ln is Y, La, Gd, Yb) to a solution of $H_2$salphen in dimethyl sulfoxide (DMSO), followed by addition of MOH (M is Li, Na, K, Cs), or (ii) addition of *o*-phenylenediamine to a solution of $M[Ln(sal)_4]$ (M is Li, Na; Ln is Y) in DMSO. The lithium and cesium salts are only slightly soluble in DMSO, except for $Li[La(salphen)_2]$, which is soluble in DMSO, as are the sodium and potassium salts. On the basis of similarities of the spectroscopic data for complexes **84** and the Ce(IV) complex **83**, the structure of the $[Ln(salphen)_2]^-$ anion in **84** was proposed to be similar to the solid-state structure of **83** [52].

Reaction of the potentially dianionic, pentadentate 2,6-pyridinediylbis[*N*-(2-hydroxyphenylaldimine)] ($H_2L^1$) or 2,5-pyrrolediylbis[*N*-(2-hydroxyphenylaldimine)] ($H_2L^2$) with $Ln(NO_3)_3$ in refluxing methanol in the absence of a




**83**

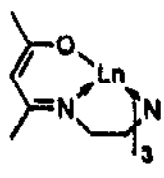
Fig. 10. Schematic representation of $Ce(salphen)_2$ (**83**).

base, was reported to afford lanthanide complexes of the mono-deprotonated ligands (**XIc**): $Ln(HL^1)(NO_3)_2{\cdot}(H_2O)_n$ (**85**; $n=1$: Ln is Pr, Gd, Dy, Er, Yb; $n=2$: Ln is Y, La, Ce) [76], $Ln(HL^2)(NO_3)_2{\cdot}(H_2O)_n$ (**86**; $n=1$: Ln is Pr, Gd, Dy, Er; $n=2$: Ln is Sc, Y, La) and the Ce(IV) complex $Ce(HL^2)(NO_3)_3{\cdot}(H_2O)_2$ (**87**) [77]. In these complexes no interaction of the pyridine and pyrrole nitrogen atoms with the lanthanide centers was observed. IR data for the complexes indicate that the second acidic hydrogen is involved in hydrogen bonding and, based on the structure of the ligand, probably held in between the two phenolate oxygen atoms (see **XIc**). Complexes **85** are soluble in water and DMF, and decompose between 210 and 325°C. Complexes **86** and **87** are slightly soluble in DMF, DMSO and nitrobenzene, and decompose between 230 and 340°C.

Trianionic polydentate ligands are very rare in lanthanide chemistry, but of interest with respect to their potential application as magnetic resonance contrasting agents, for which purpose water-soluble, neutral complexes are required [78]. Complexes Ln(trac) (**88**; trac is tris(3-aza-4-methyl-6-oxohept-4-en-1-yl)amine; Ln is La, Sm, Er, Yb), Ln(hatren) (**89**; hatren is tris(((2-oxobenzyl)imino)ethyl)amine; Ln is La, Sm, Yb) and Ln(datren) (**90**; datren is tris(((2-oxo-4,5-dimethylbenzyl)imino)ethyl) amine; Ln is La, Sm, Yb) (**XId–XIe**) were synthesized by reaction of $Ln[N(SiMe_3)_2]_3$ with the appropriate trisalkoxide or trisphenol in THF at room temperature [79]. Complexes **88–90** are very unstable towards moisture and strong $\sigma$-donor solvents like DMSO and pyridine; this was attributed to either metal-enhanced hydrolysis of the ligand in water or solvent competition. The solubility of the complexes in THF decreases in the order Ln(trac) ≫ Ln(hatren) > Ln(datren). Complexes **88** for Ln is Sm, Er and Yb are thermally robust and sublime intact. The crystal structure of Yb(trac) shows all seven donor sites of the trianionic ligand to coordinate to the ytterbium center in a monocapped distorted octahedron with the apical amino functionality capping the face formed by the three imine functionalities (see Fig. 11) [79].

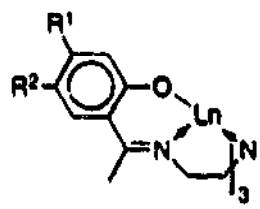
**Type XI**
**(continued)**
**acyclic, polydentate alkoxide- and phenolate-based ligands**

**d**



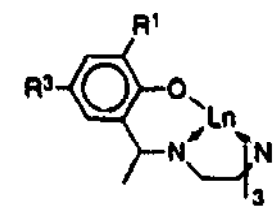
**trac**

**e**



**hatren:** $R^1 = R^2 = H$.
**datren:** $R^1 = R^2 = Me$.

**f**



$L^3$: $R^1 = H$; $R^2 = H$
$L^4$: $R^1 = H$; $R^2 = Cl$.
$L^5$: $R^1 = H$; $R^2 = Br$.
$L^6$: $R^1 = OMe$; $R^2 = H$.

Similar complexes that are stable towards hydrolysis were obtained by reduction of the imine HC=NR functionality (in complexes **XIe**) to the more stable amine $CH_2$-NH(R) functionality (in complexes **XIf**). These amine phenolate complexes

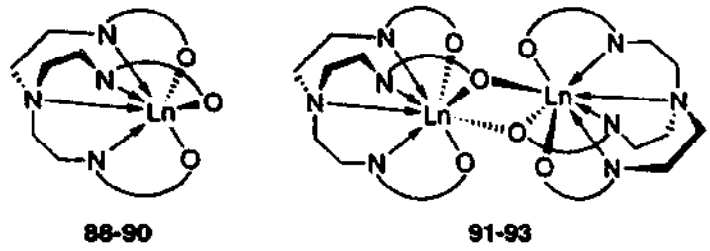
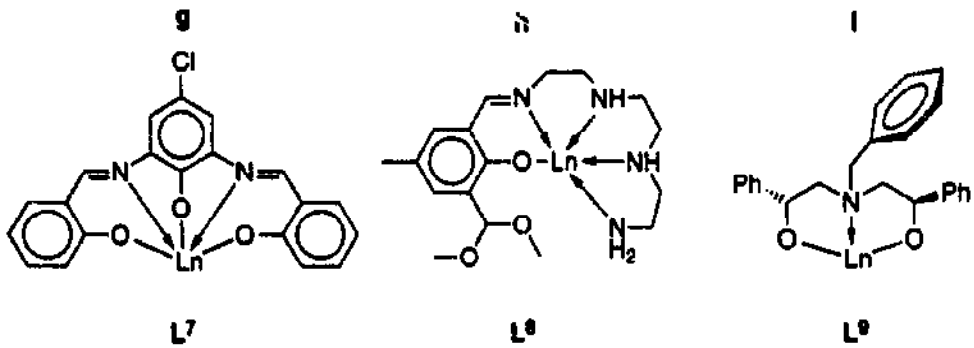



Fig. 11. Schematic representations of the monomeric complexes **88–90** and the dimeric complexes **91–93**, showing the arrangement of the neutral and anionic donor atoms around the metal centers.

$[Ln(L^3)]_2$ (**91**; $L^3$ is tris(((2-oxobenzyl)amino)ethyl)amine; Ln is Y, La, Pr, Nd, Gd, Dy), $[Ln(L^4)]_2$ (**92**; $L^4$ is tris(((2-oxo-5-chlorobenzyl)amino)ethyl)amine; Ln is La, Gd) and $[Ln(L^5)]_2$ (**93**; $L^5$ is tris(((2-oxo-5-bromobenzyl)amino)ethyl)amine; Ln is La, Nd, Gd) were prepared by reaction of $Ln(NO_3)_3$ with the appropriate amine phenol ligands ($H_3L^3$, $H_3L^4$ or $H_3L^5$) in methanol/water or methanol/chloroform/water in the presence of a base [80]. These complexes are insoluble in common organic solvents. In contrast to the imine phenolate complexes **88–90**, the amine phenolate complexes **91–93** are dimeric species, as was indicated by the FAB mass spectra of the complexes and firmly established by the crystal structure of $[Gd(L^3)_2]\cdot(CHCl_3)_2$. This structure shows that each heptadentate ligand coordinates with all donor sites to one gadolinium and bridges with one phenolate oxygen to the other gadolinium center, resulting in two eight-coordinate metal centers (see Fig. 11). Apparently, the more flexible ligand backbone, as compared to the imine complexes **88–90**, reduces the steric shielding of the lanthanide ions and results in the observed formation of dimeric species. This is supported by the characterization of the monomeric complex $Gd(L^6)$ (**94**; $L^6$ is tris(((2-oxo-3-methoxybenzyl)amino)ethyl)amine), a small amount of which could be obtained pure in the initial stage of the reaction of $Gd(NO_3)_3$ with $H_3L^6$ in methanol/chloroform/water in the presence of six to eight equivalents of NaOH [81]. Further work-up of the reaction mixture afforded a mixture of **94** and $[Gd(H_3L^6)_2](NO_3)_3$. The FAB mass spectra confirmed that **94** is a monomeric species, which can be attributed to increased (as compared with **91–93**)

**Type XI**
**(continued)**
**acyclic, polydentate alkoxide- and phenolate-based ligands**



steric shielding of the metal center by the *ortho*-methoxy substituents. No analytically pure complexes similar to **94** could, however, be isolated for Ln is Pr, Nd and Yb.

Another example of a trianionic ligand is represented by $L^7$ (**XIg**), where the three phenolate oxygen donors are held in much closer proximity than in complexes **88–94** (**XId–XIf**). Complexes $Ln(L^7)(H_2O)_n$ (**95**; Ln is La, Pr, Sm, Gd, Dy, Yb) were prepared by reaction of $H_3L^7$ with the appropriate lanthanide nitrate in the presence of three equivalents of a base (LiOH) [82]. It was recognized that pentacoordination of the ligand to the lanthanide centers is difficult in view of the ligand backbone, and, even if this does occur, the limited number of solvent molecules present still indicates that oligomerization probably takes place. Unfortunately, no further data were reported.

DMSO-soluble complexes of $L^8$ (**XIh**), general formula $Ln(L^8)(NO_3)_2X$ (**96**; Ln is Pr, X is MeOH; Ln is La, Nd, X is $H_2O$), were prepared by a template procedure, involving low-temperature (0°C) acid-catalyzed condensation of 2,6-diformyl-*p*-cresol and triethylenetetramine (1:2 ratio) with $Ln^{3+}$ as the template [83]. As a result of the mild acidic conditions, the non-condensed carbonyl function has been acetalized. The X-ray structure of $Pr(L^8)(NO_3)_2(MeOH)$ shows the ligand to be oxygen-bonded, with all four nitrogen donor functionalities coordinating to the lanthanide center. In combination with two bidentate coordinating nitrate anions and a coordinating molecule methanol, this amounts to a ten-coordinate metal center.

Complexes [(*R*,*R*)-$L^9$]LnI (**97**; **XIi**), prepared by reaction of [(*R*,*R*)-$L^9$]$Li_2$ with $SmI_3$ in THF, appear to be excellent catalysts for asymmetric Meerwein–Ponndorf–Verley reductions [84]. For example, the reduction of simple aryl methyl ketones using **97** (Ln is Sm) gave the (*R*)-alcohols with enantiomeric excesses of 92% or more. Optimal selectivities were found with Ln is Tb, Sm, Nd, while elements with either larger or smaller ionic radii gave lower enantioselectivities. Non-linear effects were observed with respect to the correlation of the e.e. of the catalyst and the e.e. of the corresponding product, which was interpreted as an indication for aggregation of the catalyst in solution [84].

### *4.3. Complexes of macrocyclic ligand systems (Table 5)*

The preparation and elucidation of the structure of both homo- and heterodinuclear lanthanide complexes[3] of macrocycles (Mcs) is of particular interest with respect to lanthanide metal-to-metal interactions [86] (cross-relaxation processes) [87a,88] and their applications in lasers [87], phosphors [89], extractive metallurgy [90,91] and NMR tomography [78a], for the characterization of complex biomolecules [92], and for the preparation of atomically homogeneous precursors for oxides with well-defined electronic characteristics [93].

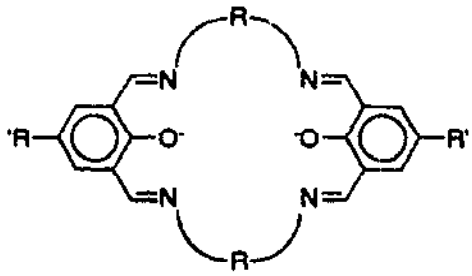
[3] For an exhaustive review on lanthanide (and actinide) complexes of macrocyclic ligands, see Ref. [85a]. For a review including lanthanide complexes of both macrocyclic and compartmental ligands, see Ref. [85b].

Table 5
Lanthanide complexes of cyclic and compartmental phenolate-based ligands

| | Complex[a] | Lanthanide metals[b] | Ln–Do bond lengths (Å) | Ligand type | Ref. |
|---|---|---|---|---|---|
| 98 | $Ln_2(Mc^1)X_{4-n}(OH)_n\cdot(H_2O)_m$ | La–Nd, Sm–Lu ($n=0$, 1, 2; X = $No_3$, $ClO_4$) | — | XII | [94] |
| 99 | $Ln_2(Mc^2)(NO_3)_4\cdot(H_2O)_n$ | La, Sm, Eu, Dy ($n=1$); Pr, Gd, Tb ($n=2$) | — | XII | [95] |
| 100 | $LnLn'(Mc^2)(NO_3)_4\cdot(H_2O)_n$[c] | LaDy, DyEu, GdTb ($n=1$); LaSm, LaGd, LaEu, LaTb, DyGd, GdEu, EuTb ($n=2$) | — | XII | [95] |
| 101 | $Ln_2(Mc^3)(NO_3)_4(H_2O)$ | La, Pr, Nd, Sm, Eu, Gd, Tb | Gd–N: 2.46, 2.70[d]<br>Gd–O: 2.57, 2.68[d] | XII | [90] |
| 102 | $Ln(Mc^4)(NO_3)\cdot(H_2O)_n$ | Gd ($n=4$), Dy ($n=3$) | — | XII | [96] |
| 103 | $Ln(Mc^5)(NO_3)\cdot(H_2O)_n$ | La ($n=4$), Dy ($n=2$) | — | XII | [96] |
| 104 | $Ln_2(Mc^6)(NO_3)_4\cdot(MeOH)_{1.2}$ | La, Pr, Nd, Eu, Tb | Pr–N: 2.707(6), 2.606(6)<br>Pr–O: 2.634(5), 2.643(5) | XII | [91] |
| 105 | $LnLn'(Mc^6)(NO_3)_4\cdot(MeOH)_{1.2}$ | $La_{0.9}Tb_{0.03}$, $La_{0.89}Eu_{0.11}$ | — | XII | [91] |
| 106 | $Ln_3(Mc^7)(OH)_2(No_3)_4\cdot(H_2O)_n$ | La, Pr, Eu, Gd ($n=4$–7) | 2.697(16)–2.880(16) | XII | [97] |
| 107 | $Ln_3(Mc^7)(OH)(NCS)_5\cdot(H_2O)_7$ | La, Pr, Eu, Gd | — | XII | [97] |
| 108 | $Ln(OH)M(CL^1)\cdot(H_2O)_n$ | M = Ni(II): La, Nd, Eu, Ho, Yb, Lu<br>M = Cu(II): La, Nd, Eu, Ho, Yb | — | XIIIa | [99] |
| 109 | $Ln(NO_3)(Ni(CL^2)\cdot(H_2O)_n$ | La, Pr, Eu | — | XIIIa | [100] |
| 110 | $Ln(CL^2(NO_3)\cdot(H_2O)_n$ | La, Ce, Pr, Nd, Sm, Eu | — | XIIIa | [100] |
| 111 | $Ln(CL^2(NO_3)\cdot(H_2O)_n$ | La, Ce, Pr, Nd, Sm | — | XIIIa | [100] |
| 112 | $Ln_2(pap)_2(NO_3)(OH)\cdot(H_2O)_n$[e] | La ($n=2$), Pr ($n=6$), Eu ($n=3$) | — | XIIIb | [100] |
| 113 | $[CuLn(Cl^4)X]_2\cdot(solv)_n$[f] | Y, La ($n=1$–4) | Y–O: 2.33(1), 2.36(1) | XIIIc | [101] |
| 114 | $Ln(LC^5)(NO_3)\cdot(H_2O)_n$ | La, Gd ($n=1$); Dy ($n=2$) | — | XIIId | [96] |
| 115 | $Ln(CL^6)(NO_3)\cdot(H_2O)_n$ | La ($n=3$), Dy ($n=2$) | — | XIIId | [96] |
| 116 | $Ln_2(CL^7)X_2\cdot(H_2O)_n$[g] | La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb | — | XIIIe | [102] |
| 117 | $Ln_2(CL^8)(NO_3)_2\cdot(H_2O)_4$ | La | — | XIIIe | [102] |
| 118 | $Ln_2(CL^9)X_2\cdot(solv)_4$[g] | La, Sm | — | XIIIe | [102] |
| 119 | $Ln_2(CL^{10})(NO_3)_2\cdot(H_2O)_n$ | Eu ($n=1$), Tb ($n=2$) | — | XIIIe | [102] |
| 120 | $Ln_2(CL^{11})(NO_3)_2\cdot(MeOH)_4$ | La | — | XIIIe | [102] |
| 121 | $Ln(CL^7)(NO_3)$ | La | — | XIIIe | [102] |
| 122 | $LnLn'(CL^{10})(NO_3)_2\cdot(H_2O)_n$ | LaEu ($n=1$), EuTb ($n=2$) | — | XIIIe | [102] |
| 123 | $LnLn'(CL^{11})(NO_3)_2\cdot(MeOH)_2$ | LaTb | — | XIIIe | [102] |

[a] Mc = Macrocycle, CL = Compartmental ligand; for ligand numbering, see figures in text. [b] Underlining indicates that a crystal structure is available. [c] Ln : Ln' = 50 : 50 (all combinations) or 99 : 1 (GdEu, TbEu, GdTb). [d] Average esd = 0.02 Å. [e] pap = dianion of 2-propionoacetylphenol. [f] X = $NO_3$, Cl; solv = $H_2O$, MeOH, DMSO. [g] X = $NO_3$, Cl, solv = $H_2O$, MeOH.

**Type XII**
cyclic, polydentate phenolate-based ligands



**Mc¹**: R = $(CH_2)_2NH(CH_2)_2NH(CH_2)_2$; R' = Me.
**Mc²**: R = $(CH_2)_2O(CH_2)_2O(CH_2)_2$; R' =Cl.
**Mc³**: R = $(CH_2)_2O(CH_2)_2O(CH_2)_2$; R' = Me.
**Mc⁴**: R = $(CH_2)_2NH(CH_2)_2$; R' = Cl.
**Mc⁵**: R = $(CH_2)_2S(CH_2)_2$; R' = Cl.

Complexes of dianionic phenolate-based macrocycles can either be synthesized via
(i) a template procedure: condensation of 2,6-diformyl-4-R'-phenol and the appropriate poly- or diamine with $Ln^{3+}$ as the template [90,94,95], or
(ii) by reaction of the preformed ligand with a lanthanide salt in the presence of a base [82,95].

Some of complexes $Ln_2(Mc^1)(X)_{4-n}(OH)_n(H_2O)_m$ (**98**; X is $NO_3$, $ClO_4$; $n=0$, 1, 2; Ln is La–Nd, Sm–Lu) were obtained in two different forms, depending on the work-up employed; as a yellow or orange microcrystalline precipitate or as a flaky off-white crystalline precipitate [94]. As the off-white complexes were increasingly difficult to prepare with decreasing $Ln^{3+}$ radius, a coordination geometry as represented by **B** (see Fig. 12) was tentatively proposed for these complexes. The coordination geometry represented by **A** was tentatively proposed for the orange compounds. Using the macrocycle $Mc^2$, both the homodinuclear complexes $Ln_2(Mc^2)(NO_3)_4(H_2O)_n$ (**99**; $n=1$: Ln is La, Sm, Eu, Dy; $n=2$: Pr, Gd, Tb) and the heterodinuclear complexes $LnLn'(Mc^2)(NO_3)_4(H_2O)_n$ (**100**; LnLn' is LaSm, LaEu, LaGd, LaTb, LaDy, GdEu, GdTb, DyEu, DyGd, EuTb) were obtained [95]. These complexes are slightly soluble in chloroform, dichloromethane and methanol, and soluble in warm DMSO. The heterodinuclear complexes were prepared by stepwise addition of the lanthanide nitrates and Ln:Ln' stochiometries of 99:1 (Ln is Gd or Tb, Ln' is Eu; Ln is Gd, Ln' is Tb) and 50:50 (all combinations) were studied.

From both emission spectra and luminescence it was concluded that complexes

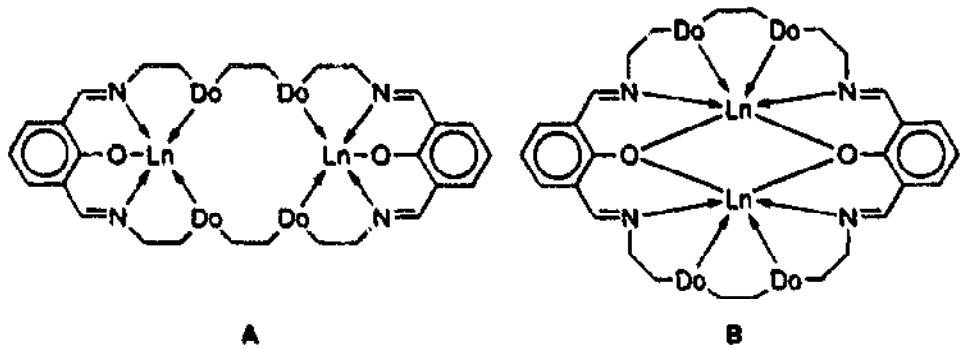
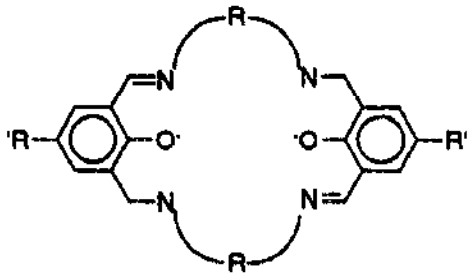



Fig. 12. The two different coordination geometries proposed for dinuclear lanthanide complexes of macrocycles.

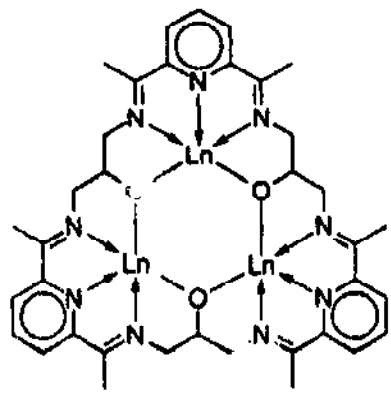
**99** and **100** are isostructural. The absence of metal–metal interactions, as concluded from the magnetic moments of the heterodinuclear complexes, indicates that the two metal ions are held far apart in their coordination environment, with no bridging heteroatom between them. This would point to a structure resembling **A** in Fig. 12. However, for the complexes $Ln_2(Mc^3)(NO_3)_4(H_2O)$ (**101**; Ln is La, Pr, Nd, Sm, Eu, Gd, Tb) of the closely related macrocycle $Mc^3$ ($Mc^2$ and $Mc^3$ differ only by the para-substituent on the aromatic nucleus) metal–metal interactions were observed and the crystal structure of the bis-gadolinium complex has the structure represented by **B**, with both phenolate oxygen atoms bridging between the two metal centers [90].

With the smaller macrocycles $Mc^4$ and $Mc^5$ the mononuclear complexes $Ln(Mc^4)(NO_3)\cdot(H_2O)_n$ (**102**; Ln is Gd ($n=4$), Dy ($n=3$)) and $Ln(Mc^5)(NO_3)\cdot(H_2O)_n$ (**103**; Ln is La ($n=4$), Dy ($n=2$)) were obtained [96]. These complexes are best synthesized by reaction of the freshly prepared ligand with the appropriate lanthanide nitrate in the presence of a base. Both ligands contain two separate pockets (analogous to the larger macrocyclic ligands mentioned above) and may be expected to be able to accommodate two lanthanide ions. However, no experiments in this direction have been mentioned for the dianionic ligands.

**Type XII**
**(continued)**
**cyclic, polydentate phenolate-based ligands**



**$Mc^6$**: R = $(CH_2)_2O(CH_2)_2O(CH_2)_2$; R' = Me



**$Mc^7$**

Because small changes in a ligand can have a significant effect on the molecular recognition process, the influence of (partial) reduction of the imine groups in $Mc^3$ to amine groups as in $Mc^6$ was also investigated [91]. Although reduction of metal-free $H_2Mc^3$ by a normal sodium tetrahydroborate procedure was expected to give a macrocycle with all imine groups reduced to amine groups, addition of $Ln(NO_3)_3\cdot(H_2O)_n$ to the tetrahydroborate reduction product did not afford the expected bis-lanthanide complexes. However, if the mixture was allowed to stand, large crystals of complexes $Ln_2(Mc^6)(NO_3)_4\cdot(MeOH)_{1,2}$ (**104**; Ln is La, Pr, Nd, Eu, Tb) were deposited [91]. These complexes apparently result from selective oxidation, in the presence of the lanthanide ions, of two of the four amine groups in the all-amine macrocycle to give the asymmetric chelate $Mc^6$. Allowing the tetrahydroborate solutions to stand without the addition of lanthanide salts appeared to lead to

oxidation of all amine groups. These observations indicate that lanthanide complexes of macrocyclic amines are considerably less stable than those of macrocyclic imines [91].

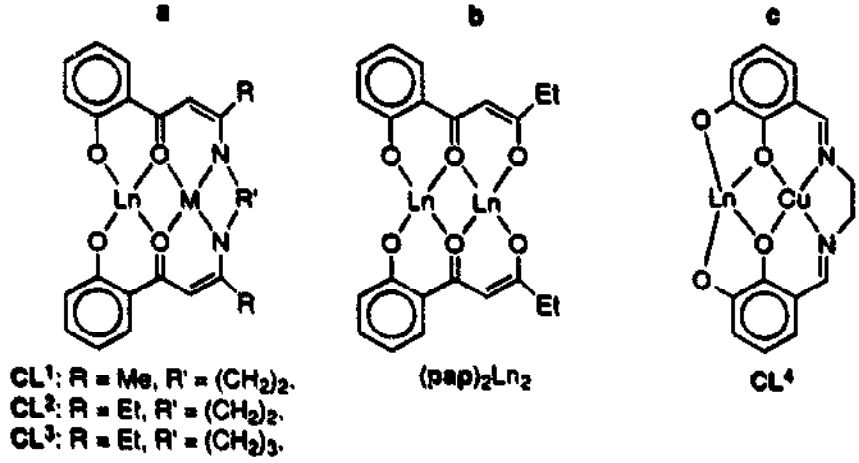
The crystal structure of $Pr_2(Mc^6)(NO_3)_4 \cdot (MeOH)_{1.2}$ is similar to that of the bis-gadolinium complex **101** (see representation **B** in Fig. 12) with the praseodymium ions bridged by the two phenolates and each coordinated by an imine nitrogen, an amine nitrogen and two oxygen atoms in one chain of the macrocycle. Two bidentate coordinated nitrate groups complete the coordination sphere on each praseodymium, leading to ten-coordinate metal centers. In addition to the homodinuclear complexes **104**, also heterodinuclear complexes $LnLn'(Mc^6)(NO_3)_4 \cdot (MeOH)_{1.2}$ (**105**; LnLn' is $La_{0.97}Tb_{0.03}$, $La_{0.89}Eu_{0.11}$) were prepared [91]. For these complexes, enrichment of $La^{3+}$ from $La_{0.8}Tb_{0.2}$ in the reaction mixture to $La_{0.97}Tb_{0.03}$ in the crystalline product was observed, indicating that macrocycle $Mc^6$ can act as a selective dinucleating agent. However, no enrichment of either lanthanide ion was observed in the LaEu complex.

The trinuclear macrocyclic complexes $Ln_3(Mc^7)(OH)_2(NO_3)_4 \cdot (H_2O)_n$ (**106**; Ln is La, Pr, Eu, Gd; $n = 4$–7) and $Ln_3(Mc^7)(OH)(NCS)_5 \cdot (H_2O)_7$ (**107**; Ln is La, Pr, Eu, Gd) were prepared by template condensation of 2,6-diacetylpyridine with 1,3-diaminopropane-2-ol in refluxing methanol with $Ln(NO_3)_3 \cdot (H_2O)_n$ and $Ln(NCS)_3 \cdot (H_2O)_n$, respectively, as the template [97]. The X-ray structure of $La_3(Mc^7)(OH)_2(NO_3)_4 \cdot (H_2O)_4$ shows the three lanthanide ions to form an approximately equilateral triangle ($La \cdot La \approx 4$ Å) with a $\mu_3$-$OH^-$ bridging between the lanthanide ions. In order to study possible metal–metal interactions a number of mixed La/Gd complexes were also prepared, but apparently not analyzed with respect to their actual structure. In any case, no conclusions could be drawn from ESR measurements with respect to metal–metal interactions.

### *4.4. Complexes of compartmental ligand systems*

Another class of ligands that is especially suited for accommodating two (different) metal centers, are the so-called compartmental ligands [98] (CLs, type **XIII**), which contain two different coordination pockets [85b].

**Type XIII**
**compartimental phenolate-based ligands**




**CL¹**: R = Me, R' = $(CH_2)_2$.
**CL²**: R = Et, R' = $(CH_2)_2$.
**CL³**: R = Et, R' = $(CH_2)_3$.

**(pap)₂Ln₂**

**CL⁴**

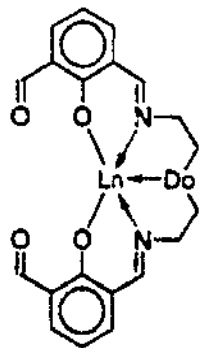
The first complexes of this type were the heterobimetallic complexes $Ln(OH)M(CL^1)(H_2O)_n$ (**108**; for M is Ni(II): Ln is La, Nd, Eu, Ho, Yb, Lu; for M is Cu(II): Ln is La, Nd, Eu, Ho, Yb) [99]. These complexes were synthesized by deprotonation of complexes $M(H_2CL^1)$ with LiOH in a pyridine/ethanol mixture, followed by the addition of the appropriate lanthanide nitrate. The complexes were reported to be only sparingly soluble or even insoluble in common solvents, with the exception of pyridine or similar coordinating solvents. Previous studies had shown that the Cu(II) and Ni(II) ions occupy the internal $N_2O_2$ pocket, leaving the outer $O_2O_2$ pocket for the lanthanide ions. Coordination of the lanthanide ions was established from IR data, and electronic spectra showed that the internal divalent cations are unaffected by the presence of the lanthanide ion in the adjacent $O_2O_2$ compartment. The closely related complexes $Ln(NO_3)Ni(CL^2)\cdot(H_2O)_n$ (**109**; Ln is La, Pr, Eu) have also been reported, in addition to the mononuclear complexes $Ln(CL^2)(NO_3)\cdot(H_2O)_n$ (**110**; Ln is La, Ce, Pr, Nd, Sm, Eu) and $Ln(CL^3)(NO_3)\cdot(H_2O)_n$ (**111**; Ln is La, Ce, Pr, Nd, Sm) [100]. The absence of the O–H and the presence of the N–H stretch vibration in the IR showed the lanthanide ions to occupy the outer $O_2O_2$ pocket in the mononuclear complexes **110** and **111**. Complexes of the dianion of 2-propionoacetylphenol (pap), $Ln_2(pap)_2(NO_3)(OH)\cdot(H_2O)_n$ (**112**; Ln is La ($n=2$), Pr ($n=6$), Eu ($n=3$)) were assigned a structure resembling that of complexes **108–111** by analogy to their transition metal analogs [100]. However, the low apparent coordination numbers (even including crystal water), as well as the possibility of dehydration mentioned for complexes **108**, make a simple monomeric structure of complexes **108–111** and a dimeric structure for complexes **112** rather unlikely. Unfortunately (or consequently), the complexes were reported to be too involatile for mass-spectral studies [100].

The mixed Cu(II)–Ln(III) complexes $[CuLn(CL^4)X]_2\cdot(solv)_n$ (**113**; Ln is Y, La; X is Cl, $NO_3$; solv is $H_2O$, MeOH; $n=1$–4) were prepared by a procedure similar to that reported for complexes **108**, using methanol as the solvent [101]. The X-ray structure of $[CuY(CL^4)(NO_3)(DMSO)]_2\cdot(DMSO)_2$ shows the complex to be dimeric in the solid state, with each yttrium occupying the outer $O_2O_2$ pocket of one ligand and coordinated by one oxygen atom of the $O_2O_2$ pocket of the other ligand, leading to a bridging $Y_2O_2$ unit. The coordination geometry around each yttrium is completed by a bidentate coordinated nitrate anion and one DMSO molecule, leading to two eight-coordinate yttrium centers. In analogy to complexes **108** and **109**, the Cu(II) ions occupy the inner $N_2O_2$ pockets. These complexes are of interest for the development of new routes for the preparation of mixed oxides for ceramic superconductor synthesis: thermogravimetric measurements showed that decomposition of the complexes eventually gave $CuLn_2O_4+CuO$ [101].

The acyclic dianionic ligands $CL^5$ and $CL^6$ are precursors for the cyclic ligands $Mc^4$ and $Mc^5$ respectively [96], and should in principle be able to accommodate two metal centers. However, only the mononuclear complexes $Ln(LC^5)(NO_3)\cdot(H_2O)_n$ (**114**; $n=1$: Ln is La, Gd; $n=2$: Dy) and $Ln(CL^6)(NO_3)\cdot(H_2O)_n$ (**115**; Ln is La ($n=3$), Dy ($n=2$)) have been reported [96]. Whether the lanthanide ion occupies the inner $N_2O_2Do$ (Do is S, NH) pocket or the outer $O_2O_2$ pocket could not be

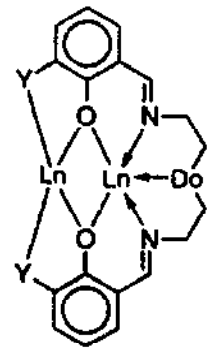
**Type XIII**
(continued)
compartimental phenolate-based ligands

d



$CL^5$: Do = NH.
$CL^6$: Do = S.

e



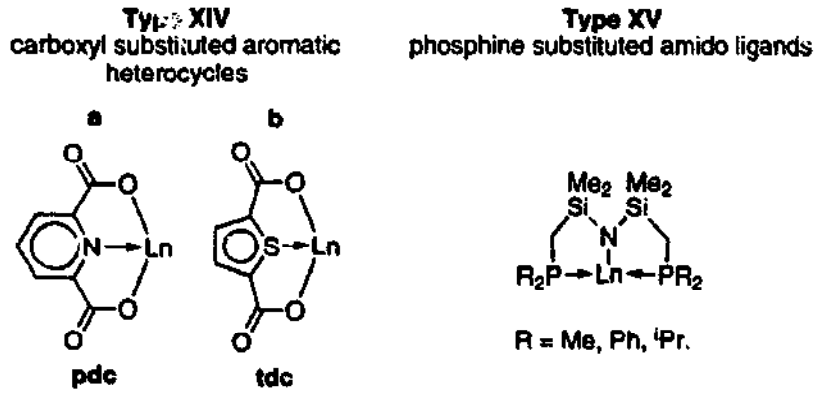
$CL^7$: Do = $N(CH_2)_{11}Me$: Y = COO.
$CL^8$: Do = $N(CH_2)_{11}Me$: Y = O.
$CL^9$: Do = NH: Y = COO.
$CL^{10}$: Do = NH: Y = O.
$CL^{11}$: Do = S: Y = O.

established from the IR data. Homo- and heterodinuclear complexes could be obtained by replacing the neutral aldehyde substituents in $CL^5$ and $CL^6$ by anionic substituents as in the ligands $CL^7$–$CL^{11}$. The homodinuclear complexes $Ln_2(O_4N_2Do)X_2 \cdot (solv)_n$ (**116**: $O_4N_2Do$ is $CL^7$; Ln is La, Pr, Nd, Sm–Dy, Yb; X is $NO_3$, Cl; solv is $H_2O$; **117**: $O_4N_2Do$ is $CL^8$; Ln is La; X is $NO_3$; solv is $H_2O$; **118**: $O_4N_2Do$ is $CL^9$; Ln is La, Sm; X is $NO_3$, Cl; solv is $H_2O$, MeOH; **119**: $O_4N_2Do$ is $CL^{10}$; Ln is Eu, Tb; X is $NO_3$; solv is $H_2O$; **120**: $O_4N_2Do$ is $CL^{11}$; Ln is La; X is $NO_3$; solv is MeOH) were prepared by a template procedure, analogous to the lanthanide complexes of macrocycles (vide supra) [102]. The long aliphatic chains present on the ligand in complexes **116** and **117** were introduced in an attempt to increase the solubility of these complexes in organic solvents, but probably as a result of oligo- or polymerization this was not successful [102].

IR data for the only mononuclear complex that could be isolated, $La(H_2O_4N_2Do)(NO_3)$ (**121**; $O_4N_2Do$ is $CL^7$), showed the lanthanide ion to occupy the outer $O_2O_2$ pocket [102], analogous to complexes **110** and **111**. The heterobimetallic complexes $LnLn'(O_4N_2Do)(NO_3)_2 \cdot (solv)_n$ (**122**; $O_4N_2Do$ is $CL^{10}$; LnLn' is LaEu, EuTb; solv is $H_2O$; **123**: $O_4N_2Do$ is $CL^{11}$; LnLn' is LaTb; solv is MeOH) were prepared by a stepwise procedure: to the in situ prepared ligand, $Ln(NO_3)_3 \cdot (H_2O)$ is added with formation of $Ln[H_4(O_4N_2Do)](NO_3)_3$, followed by successive addition of four equivalents of LiOH and $Ln'(NO_3)_3 \cdot (H_2O)$ [102]. The homogeneity and monomeric nature in these complexes were established by electron microscopy in combination with X-ray fluorescence analysis. It was reasoned that the complexes are most probably dimeric in structure, analogous to the CuY complex **113**. There were indications for metal–metal interactions through the bridging atoms in the complex $Gd_2(O_4N_2Do)(NO_3)_2 \cdot (H_2O)_4$.

## 5. Miscellaneous (Table 6)

Although a wide range of lanthanide chelate complexes of (poly)carboxylic acids containing donor functionalities [(poly)aminepolycarboxylates] have been studied, most attention has been paid to formation constants in aqueous solution, and to heats and entropies of formation [103]. Relatively little is known of the actual structures of most of these complexes [103] and they have therefore been excluded from this overview.



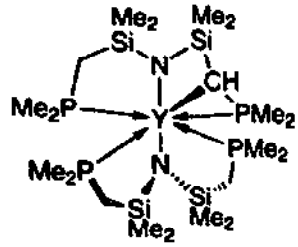

An exception is made for the lanthanide complexes of pyridine-2,6-dicarboxylate (pdc) and thiophene-2,5-dicarboxylate (tdc) (**XIV**). Complexes $Ln(pdc)(Hpdc)\cdot(H_2O)_n$ (**124**; Ln is La ($n=6$), Gd ($n=8$), Dy ($n=6$)) and $Na_3[Ln(pdc)_3]\cdot(H_2O)_m$ (**125**; Ln is La, Gd, Dy) were prepared by reacting $Ln(NO_3)_3$ with $H_2pdc$ in water in the presence of NaOH with $Ln/H_2pdc/NaOH$ molar ratios of 1:3:6 and 1:2:4, respectively [104]. While complexes **125** are soluble in cold water, complexes **124** are only soluble in hot water. Both types of complexes behave as electrolytes, indicating that even complexes **124** dissociate in solution. The crystal structure of $[La(pdc)(Hpdc)(H_2O)_2]\cdot(H_2O)_4$ shows both ligands to coordinate in a tridentate fashion, with one carboxyl group bridging to a second lanthanum, forming a polymeric chain. Two coordinated water molecules complete the coordination sphere around lanthanum, leading to a nine-coordinate metal center. With thiophene-2,5-dicarboxylate, complexes $Ln_2(tdc)_3\cdot(H_2O)_n$ (**126**; Ln is La, Gd, Dy) and $Ln(tdc)(OH)\cdot(H_2O)$ (**127**; Ln is Sm, Gd) were obtained, which were insoluble in common organic solvents [104].

Some of the very few known examples of phosphine-stabilized complexes of Group 3 and lanthanide metals (see also complexes **45** and **59**) are the bis(amido-diphosphine) complexes (**XV**) $LnCl[N(SiMe_2CH_2PR_2)_2]_2$ (**128**: R is Me, Ln is Y, La, Lu; **129**: R is Ph, Ln is Y, La; **130**: R is $^iPr$, Ln is Y) [105]. These complexes were synthesized by reaction of $LnCl_3$ with two equivalents of $MN(SiMe_2CH_2PR_2)_2$ (M is Li (Ln is Y, Lu), K (Ln is La)) in THF at room temperature. The complexes are soluble in THF and aromatic and aliphatic solvents. Substitution of chloride in complexes **128** was only successful using PhLi or $PhCH_2K$ for the yttrium and lutetium complexes, with formation of $LnR[N(SiMe_2CH_2PMe_2)_2]_2$ (**131**: R is Ph, Ln is Y, Lu; **132**: R is $PhCH_2$, Ln is Y) [105c]. These complexes are thermally

Table 6
Lanthanide complexes of miscellaneous ligands containing intramolecularly coordinating substituents

| | Complex | Lanthanide metals[a] | Ln–Do bond lengths (Å) | Ligand type | Ref. |
|---|---|---|---|---|---|
| 124 | $Ln(pdc)(Hpdc)\cdot(H_2O)_n$[b] | La, Dy ($n=6$); Gd ($n=8$) | La–N: 2.67[c] | XIVa | [104] |
| 125 | $Na_3[Ln(pdc)_3]\cdot(H_2O)_n$[b] | La, Gd, Dy | — | XIVa | [104] |
| 126 | $Ln_2(tdc)_3\cdot(H_2O)_n$[d] | La, Gd, Dy | — | XIVb | [104] |
| 127 | $Ln(tdc)(OH)\cdot H_2O$[d] | Sm, Gd | — | XIVb | [104] |
| 128 | $LnCl[N(SiMe_2CH_2PMe_2)_2]_2$ | Y, La, Lu | — | XV | [105] |
| 129 | $LnCl[N(SiMe_2CH_2P(Ph)_2)_2]_2$ | Y, La | — | XV | [105] |
| 130 | $LnCl[N(SiMe_2CH_2P(^iPr)_2)_2]_2$ | Y | — | XV | [105] |
| 131 | $LnPh[N(SiMe_2CH_2PMe_2)_2]_2$ | Y, Lu | — | XV | [105c] |
| 132 | $Ln[CH_2Ph][N(SiMe_2CH_2PMe_2)_2]_2$ | Y | — | XV | [105c] |
| 133 | $Ln[N(SiMe_2CHPMe_2)_2][N(SiMe_2CH_2PMe_2)_2]$ | Y, La, Lu | Y–P: 2.817(3), 2.896(3), 2.903(3), 3.005(3) | XV | [105c] |
| 134 | $Ln[P(C_6H_4OMe\text{-}2)_2]_3\cdot(C_6H_5Me)_n$ | Y ($n=0$), La ($n=2$) | — | XVI | [106] |
| 135 | $Ln[N(^iPr)_2][P(C_6H_4OMe\text{-}2)_2]_2\cdot(THF)(C_6H_5Me)$ | La | — | XVI | [106] |
| 136 | $[N(^iPr)_2]_2Ln[\mu\text{-}P(C_6H_4OMe\text{-}2)_2]_2Li(THF)$ | La | La–O: 2.787(9) | XVI | [106] |
| 137 | $(C_5Me_5)Ln[S_2P(OMe)_2]_2$ | Sm | Sm–O: 2.645(3) | XVII | [107] |
| 138 | $Ln(DAC)[N(SiMe_3)_2]$[e] | Y, Ce, Sm | Y–O: 2.457(12), 2.467(11), 2.514(12), 2.590(12) | XVIII | [108] |
| 139 | $Ln\{(\mu\text{-}DAC)Ln[N(SiMe_3)_2]\}_2$[e] | Yb | Yb–O: 2.49(2)–2.57(3) | XVIII | [108] |
| 140 | $\{Ln[N(SiMe_3)_2]\}_2(\mu\text{-}DAC)$[f] | Yb[c] | — | XVIII | [108] |
| 141 | $Ln(DAC)(CH_2SiMe_3)$[f] | Y | Y–O: 2.431(12), 2.442(13), 2.534(11), 2.622(11) | XVIII | [109] |

[a] Underlining indicates that a crystal structure is available. [b] pdc = pyridine-2,6-dicarboxylate. [c] No esd given. [d] tdc = thiophene-2,5-dicarboxylate. [e] DAC = deprotonated 4,13-diaza-18-crown-6. [f] As a result of extensive disorder, only the general structure is reported.



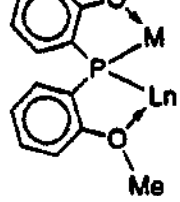

133

Fig. 13. Schematic structure of the cyclometallated complex 133.

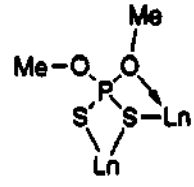
unstable, and undergo a cyclometallation reaction via abstraction of a methylene proton from the ligand backbone with liberation of benzene (complexes **131**) or toluene (complex **132**). In the case of reaction of the lanthanum complex $LaCl[N(SiMe_2CH_2PMe_2)_2]_2$ (**128**) with PhLi, only the cyclometallated complex was obtained. Coordination of the phosphine donor substituents to the lanthanide metals was established from $^1H$, $^{13}C$ and $^{31}P$ NMR. All complexes are fluxional in solution at room temperature. At low temperature all four phosphine donors are coordinated to the metal center in the case of complexes **128**, **131** and **132**.

For the complexes with phenyl substituents on phosphorus (**129**), steric crowding results in one donor remaining pendant for the yttrium complex, while the larger ionic radius of $La^{3+}$ appears to result in a monomer–dimer equilibrium at low temperature. The cyclometallated complexes $Ln[N(SiMe_2CHPMe_2)_2][N(SiMe_2CH_2PMe_2)_2]$ (**133**; Ln is Y, La, Lu) are also fluxional in solution at room temperature, and, at low temperature, coordination of all four phosphine donors was established by $^{31}P$ NMR for the yttrium and lutetium complexes. The crystal structure of $Y[N(SiMe_2CHPMe_2)_2][N(SiMe_2CH_2PMe_2)_2]$ also shows all four phosphine donors to be coordinated, resulting in a seven-coordinate metal center (see Fig. 13). Unfortunately, no reactivity was observed for the cyclometallated complexes: the cyclometallation is reversible at high temperatures under about 4 atm $H_2$ or $D_2$, but the complexes only activate their own C–H bonds [105c].

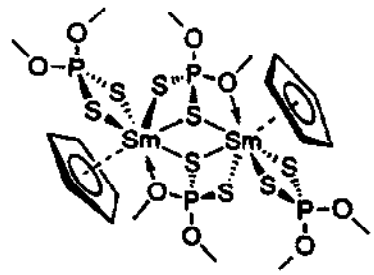
**Type XVI**
donor substituted phosphide ligands




**Type XVII**
donor substituted dithiophosphinate ligands




The only reported donor-substituted phosphide ligand used in lanthanide chemistry thus far is the bis(2-methoxyphenyl)phosphide ligand (**XVI**). The toluene-soluble complexes $Ln[P(C_6H_4OMe\text{-}2)_2]_3\cdot(C_6H_5Me)_n$ (**134**; Ln is Y ($n=0$), La ($n=2$)) were prepared by reaction of $Ln[N(^iPr)_2]_3(THF)$ with three equivalents of



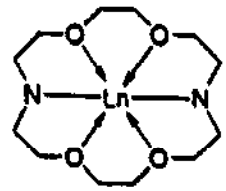
137

Fig. 14. Schematic representation of complex **137**.

$P(C_6H_4OMe\text{-}2)_2H$ in toluene at room temperature [106]. Addition of one equivalent of $P(C_6H_4OMe\text{-}2)_2H$ to $La[N(^iPr)_2]_3(THF)$ also gave complex **134** as the only product, together with unreacted lanthanide amide. However, if the reaction is performed at 0°C, bright yellow crystals of $La[N(^iPr)_2][P(C_6H_4OMe\text{-}2)_2]_2(THF)(C_6H_5Me)$ (**135**) are precipitated with virtually no formation of **134**. Reaction of $Li\{La[N(^iPr)_2]_4\}$ with two equivalents of $P(C_6H_4OMe\text{-}2)_2H$ gave good-quality crystals of $[N(^iPr)_2]_2La[\mu\text{-}P(C_6H_4OMe\text{-}2)_2]_2Li(THF)$ (**136**) [106]. The crystal structure of this complex shows the phosphide ligands to bridge La and Li through the phosphorus atom, with each of the methoxy substituents coordinating to one of the metal centers. The coordination sphere around lanthanum is completed by two dialkylamido groups, resulting in a relatively low coordination number of six.

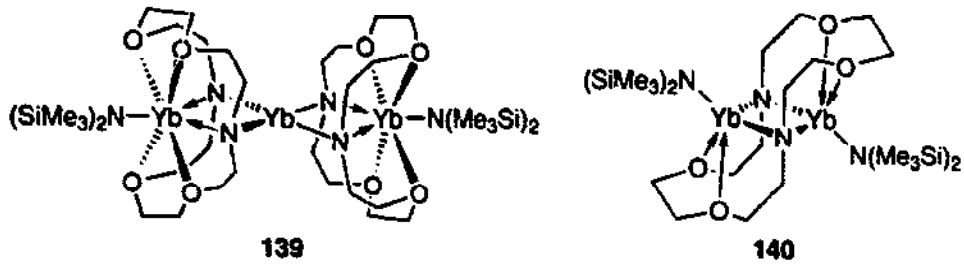
Complex $(C_5Me_5)Sm[S_2P(OMe)_2]_2$ (**137**), which was prepared by reaction of two equivalents of the divalent samarium complex $(C_5Me_5)_2Sm(THF)_2$ with $[(MeO)_2P(S)S]_2$ at room temperature in toluene [107], is another example of the incorporation of potential donor sites in relatively simple ligands. The X-ray structure shows the *O,O'*-dimethyldithiophosphate ligands to be present in two different coordination geometries: two terminally ($\eta^2$-S,S)Sm bonded ligands with both methoxy substituents pendant and two bridging Sm($\eta^2$-S,S/$\eta^1$-S)Sm ligands, each with one methoxy substituent coordinating to one of the samarium centers (see Fig. 14). Thus, the formal coordination number for the samarium centers is nine.

**Type XVIII**
**deprotonated diazacrown ethers**



**DAC**

Despite the fact that lanthanide complexes of both crown ethers and their N-substituted analogs (aza-crowns) have been extensively studied, to date only two reports on the use of deprotonated aza-crowns have appeared [108,109]. By reacting $Ln[N(SiMe_3)_2]_3$ with one equivalent of 4,13-diaza-18-crown-6 ($H_2DAC$; **XVIII**) at




139 140

Fig. 15. Schematic representations of complexes **139** and **140**, containing the DAC ligand.

room temperature in toluene, complexes Ln(DAC)[$N(SiMe_3)_2$] (**138**; Ln is Y, Ce) were obtained [108]. NMR data for the yttrium complex indicate a monomeric structure, which was confirmed by the X-ray structure of the complex. The crystal structure shows the DAC ligand to span one hemisphere of the yttrium ion as a hexacoordinate ligand, with the bis(trimethylsilyl)amido ligand shielding the space above. Complexes **138** are moderately soluble in hexane and very soluble in THF, diethyl ether and toluene. Attempts to replace the amido ligand by phenolate or alkoxide ligands were not successful. Reaction of the divalent complex Yb[$N(SiMe_3)_2$]$_3$($Et_2O$)$_2$ with $H_2$DAC in a 2:3 ratio gave complex Yb{($\mu$-DAC)Yb[$N(SiMe_3)_2$]}$_2$ (**139**), while a 2:1 ratio afforded {Yb[$N(SiMe_3)_2$]}$_2$($\mu$-DAC) (**140**) [108]. The X-ray structure of complex **139** shows each of the DAC ligands to be hexacoordinated to one ytterbium ion, which also bear one amido ligand each and are seven-coordinate. The third ytterbium ion is sandwiched between the two ligands and is only four-coordinate (see Fig. 15). NMR data and preliminary X-ray data for complex **140** show the DAC ligand in this case to act as a dinucleating ligand (see Fig. 15). The coordination sphere around each ytterbium is completed by an amido ligand, leading to the relatively low coordination number five.

Interestingly, reaction of divalent Sm[$N(SiMe_3)_2$]$_3$($THF$)$_2$ with $H_2$DAC in a 1:1 ratio afforded the trivalent complex Sm(DAC)[$N(SiMe_3)_2$] (**138**) [108]. Initial formation of divalent Sm(HDAC)[$N(SiMe_3)_2$], followed by reduction of the amine N–H bond, was proposed as a possible mechanism for the formation of **138**. Reaction of Y($CH_2SiMe_3$)$_3$($THF$)$_2$ with $H_2$DAC at room temperature in toluene allowed for the isolation of the first alkyl derivative, Y(DAC)($CH_2SiMe_3$) (**141**) [109]. The solid state structure of this complex resembles that of complex **138**. Complex **141** slowly decomposes in solution at room temperature, with formation of TMS. NMR data suggest that this decomposition involves metallation of the DAC ligand.

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