Chiral Lanthanide Complexes: Coordination Chemistry and Applications

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I. Introduction

The classical examples of chirality in coordination chemistry are transition-metal chelate complexes of the type [M(bidentate)$_3$] that exist in nonsuperimposable mirror image forms with propeller-like structure. Inert complexes of this type can be resolved and are indefinitely stable. In contrast, lanthanide complexes are generally very labile, showing virtually no stereochemical rigidity, and isolation of enantiomerically pure complexes that retain their stereochemistry in solution almost always demands the use of chiral ligands. Many enantiomerically pure lanthanide complexes have now been prepared and characterized, and far from being curiosities of coordination chemistry, many of these compounds have applications, e.g., as chiral shift reagents for resolving NMR spectra of chiral Lewis bases (dating back to the 1970s) and more recently (dating from

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Helen Aspinall is a native of Huddersfield, in the north of England. She migrated south to study for her B.Sc. and Ph.D. (with Dr Tony Deeming) degrees at University College London and then moved to Columbia University, NY, for a postdoctoral year with Professor Steve Lippard. On her return to the United Kingdom, she spent three years working with Professor Don Bradley at Queen Mary College London, wehre she was introduced to lanthanide chemistry. In 1986 she took up her present position as Lecturer in Inorganic Chemistry at the University of Liverpool, where she has developed her interest in lanthanide coordination chemistry, particularly its application to organic synthesis.

the early 1990s) as highly enantioselective catalysts and reagents. The design of complexes for these applications is still far from being an exact science, and the road to most of the successful applications has been strewn by many apparently suitable complexes that fail to meet the demanding requirements.

The purpose of this review is to give a survey of characterized chiral lanthanide complexes and to highlight successful applications of these compounds. In the field of enantioselective catalysis, several successful systems use in situ prepared catalysts, and these systems are included in order to highlight chiral ligands that define an effective chiral binding site at the lanthanide. In many cases parallels can be drawn with known coordination chemistry of these ligands.

The vast majority of the complexes covered in this review contain chiral ligands. However, complexes with achiral ligands are included in a few cases, e.g., some cases where spontaneous resolution occurs on crystallization or where interesting chiral coordination geometries are obtained in racemic form.

Coordination chemistry is covered in sections II−VII, and applications are covered in sections VIII−X. The review of characterized complexes is organized by ligand type: the first classification is by ligand donor atom; however, macrocyclic ligands are dealt with in one section. The main focus of this review is coordination chemistry, and so applications of chiral complexes as catalysts and reagents are organized by ligand type rather than by reaction.

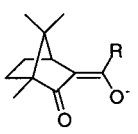
Most of the early work on lanthanide complexes focused on solution spectroscopic studies, e.g., by circular dichroism or circularly polarized luminescence spectroscopy, and this has been reviewed by Brittain.[1] This and related work (e.g., the use of achiral lanthanide complexes as CD probes for chiral substrates)[2−4] is not included in the present review.

II. Complexes with O-Donor Ligands

A. Anionic O-Donors

1. β-Diketonate Complexes

Lanthanide β-diketonates such as [Ln(thd)$_3$] (thd = Bu^{t}C(O)CHC(O)Bu^t) have been known since the early years of the 20th century, and they have been used (among other applications) as NMR shift reagents and Lewis acid catalysts. Chiral analogues have been prepared, the best known of which are camphor-derived complexes with ligands **1** and **2**, which are used as chiral NMR shift reagents (see section VIII).[5−9] These complexes also provided the first examples of enantioselective Lewis acid catalysis by a lanthanide complex (see section IX.A).



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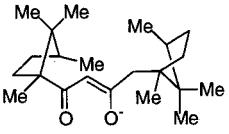
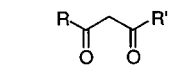


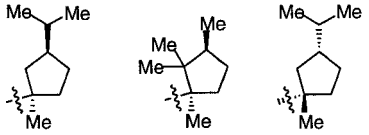
2

The crystal structure of the dimeric dmf adduct {[Pr(tfc)$_3$]$_2$(dmf)$_3$} (tfc = **1** with R = CF$_3$) has been determined.[10] Two views of the structure are shown in Figure 1.

Chiral substituents can be incorporated into the β-diketonate to give a chiral ligand. Whitesides prepared a series of chiral β-diketonate ligands (summarized below) and investigated their Eu complexes as chiral lanthanide shift reagents.[6] None of these complexes has been characterized crystallographically.

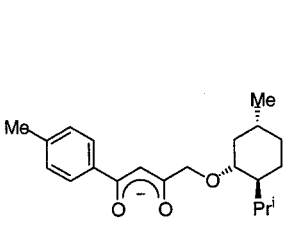


Ligand	R	R'
3	a	a
4	a	b
5	c	b
6	a	c



a **b** **c**

An L-menthyloxy-substituted β-diketonate ligand **7** has been used to prepare a chiral lanthanide tris(β-diketonate) where noncovalent interactions between ligands lock the conformation of the complex,[11] and the Gd complex has been used to catalyze the enantioselective borohydride reduction of ketones (see section IX.A).



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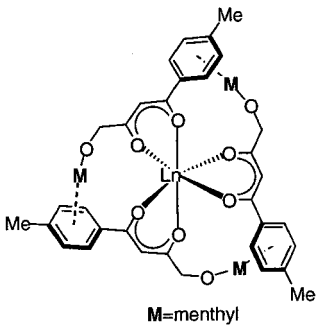


M=menthyl

2. Alkoxide Complexes

Fischer prepared a series of mixed chiral alkoxide/cyclopentadienyl complexes by reaction of [LnCp$_3$]

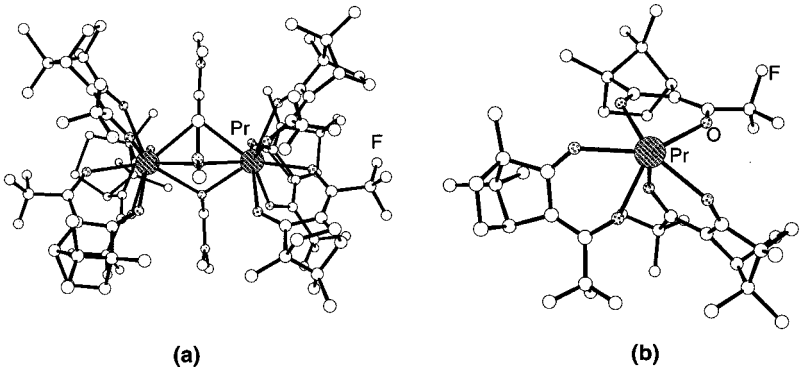
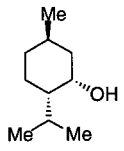


Figure 1. (a) Structure of {[Pr(tfc)$_3$]$_2$(dmf)$_3$}. (b) Structure of one [Pr(tfc)$_3$] fragment.

with 1 equiv of alcohol. Neomenthol **8** gives the dimeric complex **9** in which neomenthoxide acts as a bridging ligand.[12] Complex **9** shows CD in f−f transitions.



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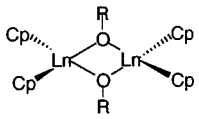

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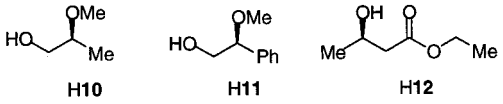
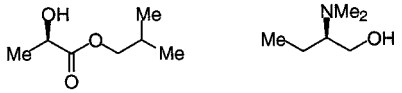
Donor-functionalized chiral alcohols H**10**−H**14** have also been investigated.[13−15]

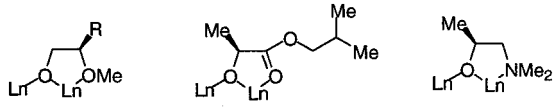


H10 **H11** **H12**



H13 **H14**

On reaction with [LnCp$_3$] these alcohols all give alkoxide-bridged complexes [Ln(μ-OR)Cp$_2$]$_2$, with the alkoxide ligands also forming chelate rings **15** to **17**.



15 **16** **17**

Several of these complexes have been characterized by X-ray diffraction, and the structure of [Cp′$_2$Yb(μ-**10**)]$_2$ (Cp′ = C$_5$H$_4$Me) is shown in Figure 2. NMR studies show that on the NMR time scale the chelate rings of Pr complexes of ligands **12** and **13** remain intact in solution; however, there is evidence for rupture of the chelate rings for Yb complexes of these ligands.[14] The Sm−N bonds of [Cp$_2$Sm(**14**)]$_2$ also rupture in solution.[15]

3. Binaphthol and Binaphtholate Complexes

Binaphthol (H$_2$binol) **18** is chiral by virtue of restricted rotation about the C−C bond linking the two naphthyl units, and the absolute configuration of *R*-binaphthol was first established unequivocally

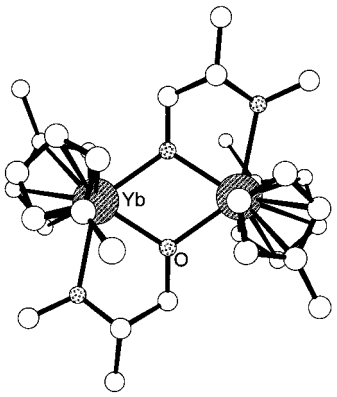
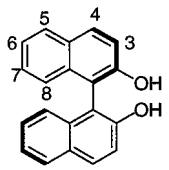


Figure 2. Structure of [Cp′$_2$Yb(μ-**10**)]$_2$ (Cp′ = C$_5$H$_4$Me).

by X-ray diffraction in 1968. The flexibility of the dihedral angle between the two naphthyl rings of this C_2-symmetric molecule allows coordination to a wide range of metal centers (examples are known from 45° to 110°), and H$_2$binol has been used as a chiral auxiliary in many metal-based enantioselective catalysts and reagents.[16]



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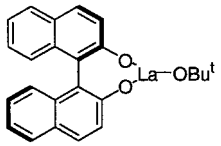
Given the known oxophilicity of the lanthanide elements, it is not surprising that binaphthol was one of the first chiral ligands to be investigated in the search for enantioselective lanthanide reagents and catalysts.

4. Complexes with Deprotonated Binaphthol

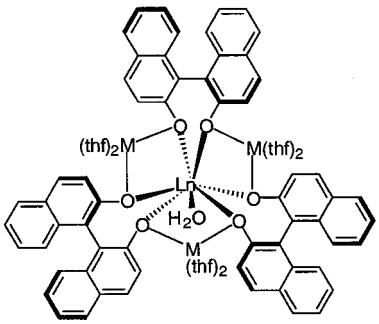
In 1992, Shibasaki reported the first enantioselective catalysis of the nitro−aldol reaction (see section IX.C).[17] The catalyst was prepared by the reaction of H$_2$binol with [La$_3$(OBu^t)$_9$] in the presence of LiCl, and its structure was tentatively proposed as **19**.

The large radii of Ln^{3+} ions and the consequent high coordination numbers suggest that this simple structure is unlikely to exist: the steric demands of binaphtholate are not sufficient to stabilize this monomeric structure. Subsequent work identified improved conditions for the synthesis of the active



19

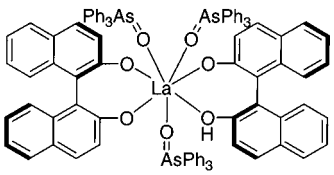
catalyst: the optimized preparation required reaction of $LnCl_3$ with Li_2binol in the presence of NaOH, Li halide, and H_2O.[18] The requirement for alkali-metal halide hinted that the structure of the catalyst was not a simple monomer as originally proposed, and in 1993 a combination of mass spectrometry and single-crystal X-ray diffraction showed the catalyst to be a heterometallic alkali-metal lanthanide tris(binaphtholate) complex.[19] The general formula of the catalyst is $[M(thf)_2]_3[Ln(binol)_3(H_2O)]$ **(20)**, and crystal structures have now been reported for $[Na(THF)_2]_3[Ln(binol)_3(H_2O)]$ (Ln = La, Pr and Eu);[20] a preliminary structure (not fully refined) of $[Li(THF)_2]_3[Sm(binol)_3(H_2O)]$ has also been reported.[21] The structure of $[Na(thf)_2]_3[Eu(S\text{-binol})_3(H_2O)]$ is shown in Figure 3.



20

The complexes have C_3 symmetry, with the Ln ion sitting slightly above (approximately 0.4 Å) the plane of the three alkali-metal ions, and the H_2O bound along the C_3 axis. As well as the chirality of the binol ligands, there is also a chiral center at the lanthanide ion. For *R*-binol complexes the stereochemistry at the Ln ion is always Δ, and conversely *S*-binol gives rise to Λ stereochemistry at Ln.

Shibasaki also used alkali-metal-free lanthanide binaphtholates in enantioselective catalysis (section IX.B). Unfortunately structural data on these catalysts has proved elusive. The crystal structure of [La(*R*-binol)(*R*-Hbinol)($Ph_3As{=}O)_3$] **(21)** has been determined, but this is not a catalytically active species.[22]



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At around the same time as Shibasaki's early work, Greeves was independently investigating the use of binaphthol as a chiral auxiliary in the enantioselective addition of organocerium reagents to aldehydes

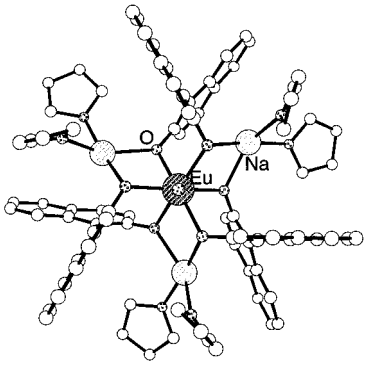


Figure 3. Structure of $[Na(thf)_2]_3[Eu(S\text{-binol})_3(H_2O)]$.

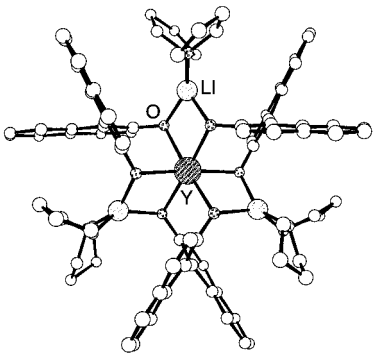


Figure 4. Structure of $[Li(thf)_2]_3[Y(R\text{-binol})_3]$.

and ketones (section X.A).[23] Again, the structure of the active reagent was originally proposed to be monomeric, but subsequent work revealed that the best enantioselectivities were achieved using 3 equiv of binaphthol per Ce. This suggested that the enantioselective organocerium reagents were analogous to the Shibasaki heterometallic catalysts, but they would have to be anhydrous in order to be compatible with the highly moisture-sensitive organometallic reagents. Anhydrous alkali-metal lanthanide binaphtholates were prepared cleanly by the protonolysis reaction of lanthanide tris(silylamides) with MHbinol (M = Na or Li).[24,25]

$$[Ln\{N(SiMe_3)_2\}_3] + 3MHbinol \xrightarrow{thf} [M(thf)_2]_3[Ln(binol)_3] + 3HN(SiMe_3)_2 \quad (1)$$

Crystal structures have been determined for $[Li(thf)_2]_3[Y(R\text{-binol})_3]$, $[Li(OEt_2)]_3[Eu(S\text{-binol})_3]\cdot[Li(OEt_2)]_3[Eu(S\text{-binol})_3(H_2O)]$, $[Li(thf)_2]_2[Li(OEt_2)][Yb(S\text{-binol})_3]$, and $[Na(thf)_2]_3[Yb(S\text{-binol})_3]$. The structure of $[Li(thf)_2]_3[Y(R\text{-binol})_3]$ is shown in Figure 4.

In solution, NMR studies show that all of the anhydrous complexes adopt D_3 symmetry, consistent with the Ln ion being coplanar with the alkali-metal ions. However, in the solid state, the Ln ion deviates significantly from the M_3 plane where M = Na but not where M = Li. The dihedral angle between the naphthyl rings of the binol ligand decreases with decreasing Ln^{3+} ionic radius (maximum values of 67° for $[Li(OEt_2]_3[Eu(S\text{-binol})_3]$ and 58.5° for $[Li(THF)_2]_2[Li(Et_2O)][Yb(S\text{-binol})_3]$).

Work on lanthanide binaphtholates has been driven by studies of enantioselective synthesis, and so it is not surprising that most work in this area has been

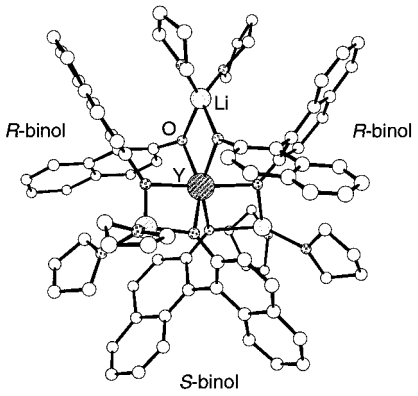
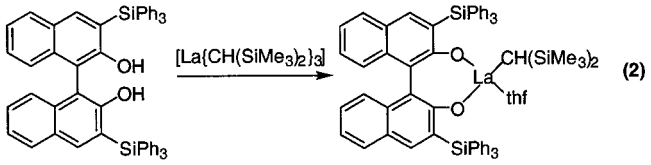


Figure 5. Structure of $[Li(thf)_2]_3[Y(R\text{-binol})(S\text{-binol})_2]$.

carried out with enantiomerically pure H_2binol. However, studies using racemic binaphthol have revealed some interesting results. Reaction of $[Y\{N(SiMe_3)_2\}_3]$ with *rac*-LiHbinol gives exclusively $[Li(thf)_2]_3[Y(R\text{-binol})(S\text{-binol})_2]$ along with its *RRS*-enantiomer, whereas reaction with *rac*-NaHbinol gives a racemic mixture of $[Na(thf)_2]_3[Y(R\text{-binol})_3]$ together with its *SSS*-enantiomer. The structure of $[Li(thf)_2]_3[Y(R\text{-binol})(S\text{-binol})_2]$ is shown in Figure 5.

Reaction of $[Yb\{N(SiMe_3)_2\}_3]$ with *rac*-NaHbinol gives a mixture of *RRR*-/*SSS*- and *RRS*-/*SSR*-$Na_3[Yb(binol)_3]$ in the ratio of ca. 3:1, as determined by NMR spectroscopy. The reasons for this selectivity in the formation of complexes from *rac*-binol are not clear; however, the 3-hydrogen of the unique binol ligand in *RRS*- and *SSR*-$Li_3[Y(binol)_3]$ interacts with the π-system of a neighboring naphthyl ring, and this interaction may stabilize the *RRS*-/*SSR*-structure. The ready formation of the *RRS*-/*SSR*-structure suggests that enantioselective catalysts and reagents should be available from binaphthol of low optical purity, leading to nonlinear effects in enantioselective reactions. A positive nonlinear effect has already been observed in the nitroaldol reaction catalyzed by lithium−lanthanum−binaphtholate.[18]

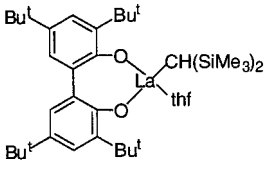
There are very few examples of mono(binaphtholate) complexes of the lanthanides; however, use of bulky Ph_3Si substituents in the 3 and 3′ positions has allowed isolation of an alkyl lanthanide binaphtholate as shown in eq 2.



(2)

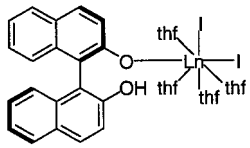
With the less sterically demanding $SiPh_2Me$ and $SiMe_3$ substituents it was not possible to isolate products. The binaphtholate complex was not characterized crystallographically, but a crystal structure has been reported for the biphenolate analogue **21a**.[26]

Collin reported the first example of a simple monodeprotonated-binaphtholate complex of a lanthanide. Reaction of KHbinol with LnI_3 (Ln = La, Sm, Yb) in thf gives $[Ln(Hbinol)I_2(thf)_4]$ **(22)**, where the OH of



21a

Hbinol is not coordinated to Ln. This complex has been characterized crystallographically.[27]



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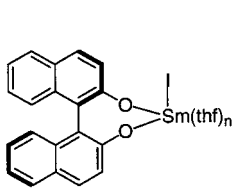
Other mono(binaphtholate) complexes **23** and **24** have been reported by Collin, but to date they have not been characterized crystallographically.[28]



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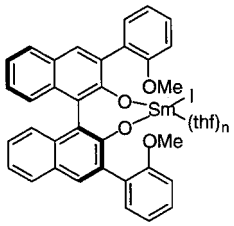


24

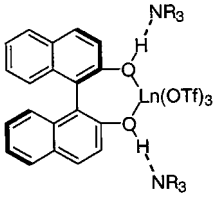
Modification of binaphthol by substitution can be achieved quite readily. Substitution at the 3 and 6 positions of the binaphthol has been investigated in catalytic reactions and will be discussed further in sections IX.B,C. These complexes have not been characterized crystallographically, and there is no indication that their structures differ grossly from those of their unsubstituted analogues.

5. Complexes with Neutral Binaphthol

Kobayashi prepared highly enantioselective catalysts by addition of H_2binol to $Ln(OTf)_3$ in the presence of a tertiary amine as shown in eq 3.

$$Yb(OTf)3 \xrightarrow{H_2\text{binol/MS 4Å}}{}^{\text{amine}}{}' \text{chiral Yb triflate}' \quad (3)$$

The catalysts have been characterized in situ by NMR and IR spectroscopy but have not been characterized crystallographically or isolated. On the basis of spectroscopic evidence the structure is proposed to be **25**.[29] These catalysts will be discussed in detail in section IX.E.



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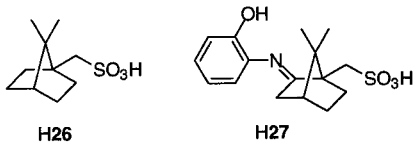
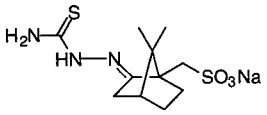
6. Camphorsulfonate Complexes

A series of lanthanide complexes derived from D-camphor sulfonic acid H**26** has been prepared. The

homomoleptic tris(camphorsulfonates) [Ln(**26**)$_3$] are prepared by reaction of H**26** with Ln(ClO_4)$_3$ in anhydrous EtOH,[30] and the heteroleptic complexes [Ln(phen)$_2$Cl(**26**)$_2$] are prepared by reaction of [Ln(phen)$_2$Cl$_3$] with Na**26**.[31] Complexes of the camphorsulfonate-derived Schiff bases **27** and **28** have also been reported; they are formulated as [Ln(H**27**)(**27**)][32] and [Ln(**28**)$_3$].[33] All of these complexes have been studied spectroscopically (including CD spectra), but none has yet been characterized crystallographically.



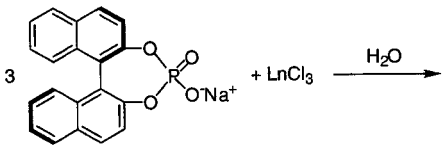
H26 H27



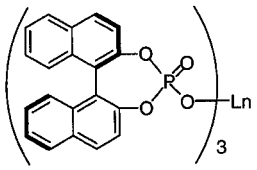
Na**28**

7. Phosphate Complexes

Lanthanide salts of the chiral binaphthol-derived phosphate BNP have been prepared by reaction of NaBNP with $LnCl_3$ in aqueous solution as shown in eq 4.[34] These complexes have been used successfully as enantioselective Lewis acid catalysts (see section IX.D).

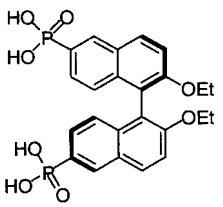


Na *R*-BNP



(4)

Another chiral ligand derived from the binaphthyl structure is the biphosphonic acid H$_4$**29**. Slow evaporation of a methanolic solution of Ln(NO_3)$_3$ or Ln(ClO_4)$_3$ with H$_4$**29** yields crystals of formula [Ln(H$_2$**29**)(H$_3$**29**)(H_2O)$_4$]·12H_2O, which have a chiral porous framework structure made up of eight-coordinate Ln centers bridged by binaphthylbisphosphonate groups.[35] The crystal structure of the *R,R*-compound has been determined, and the coordination environment of a single Gd ion in this structure is shown in Figure 6.



H$_4$**29**

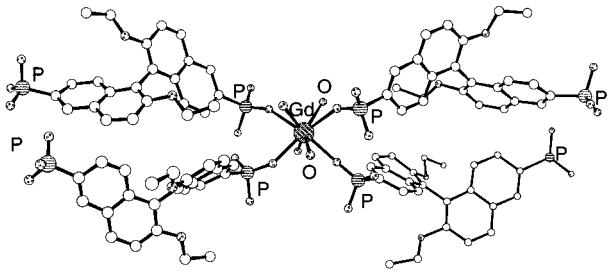
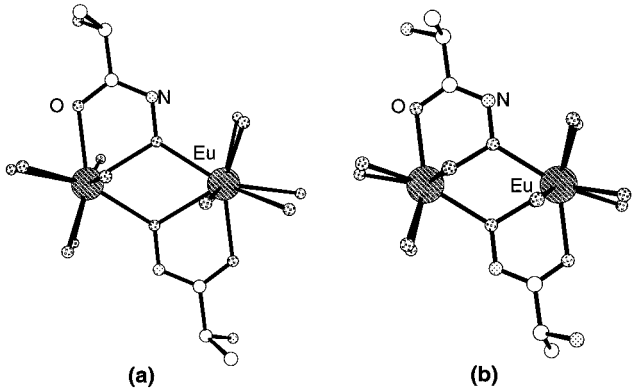


Figure 6. Coordination environment of a single Gd^{3+} ion in [Gd(*R*-H$_2$**29**)(*R*-H$_3$**29**)(H_2O)$_4$]·12H_2O.



(a) (b)

Figure 7. Structures of (a) D,L-[Eu_2(alaninehydroxamic acid)$_2$(H_2O)$_{10}$]$^{6+}$ and (b) L,L-[Eu_2(alaninehydroxamic acid)$_2$(H_2O)$_{10}$]$^{6+}$.

The presence of both Lewis and Brønsted acid sites in the structure allows catalysis of a range of organic transformations; however, no enantioselectivity has yet been achieved in these reactions. A small degree of enantioselectivity (up to 13.6%) has been achieved in the separation of racemic *trans*-1,2-diaminocyclohexane.

8. Amino Acid Complexes

Several lanthanide complexes with α-amino acids[36−40] and α-aminohydroxamic acids[41,42] have been characterized crystallographically. The amino acid acts as a bridging ligand, and the structures fall into three general classes: dimeric [Ln_2(amino acid)$_2$(H_2O)$_n$]$^{6+}$, dimeric [Ln_2(amino acid)$_4$(H_2O)$_n$]$^{6+}$, and polymeric [Ln(amino acid)$_3$(H_2O)$_n$]$_\infty^{3+}$. Examples of these structural types are shown in Figures 7−9. A polymeric chain complex [Er(proline)(H_2O)$_4$]$_n^{3+}$ has also been reported.

B. Neutral O-Donors

The chelate rings formed when polyether ligands RO(CH_2CH_2O)$_n$R (or their cyclic crown ether analogues) bind to a lanthanide can make the resulting complex chiral. These chelate rings invert rapidly in solution; however, spontaneous resolution has been observed in some cases where the complexes crystallize in noncentrosymmetric space groups. [SmI_2(dme)$_3$] (dme = dimethoxyethane) is the first eight-coordinate complex reported to undergo spontaneous resolution,[43] and a similar observation has been made for [EuI_2(dme)$_3$].[44] The structure of Λ(*δδδ*)-[SmI_2(dme)$_3$] is shown in Figure 10. [Eu(15-crown-5)(NO_3)$_3$] is an example of a crown ether complex that crystal-

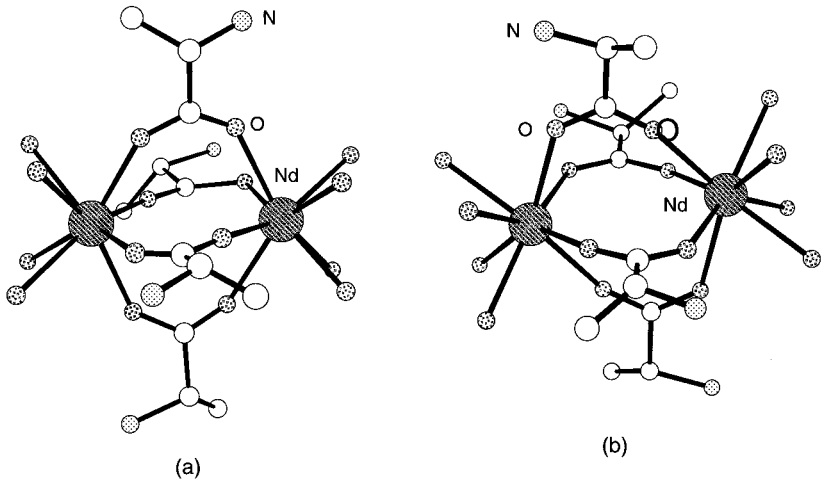


Figure 8. Structures of (a) $[Eu_2(l\text{-alanine})_4(H_2O)_8]^{6+}$ and (b) $[Eu_2(l\text{-alanine})_2(d\text{-alanine})_2(H_2O)_8]^{6+}$.

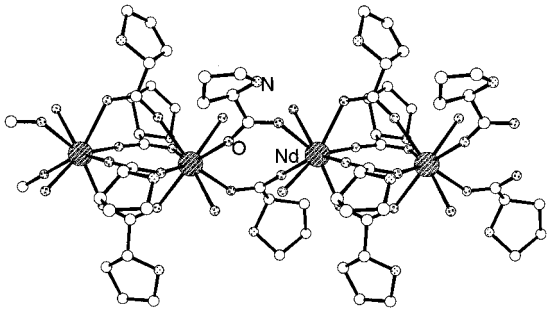


Figure 9. Structure of $[Nd(l\text{-proline})_3(H_2O)_2]^{3+}{}_n$.

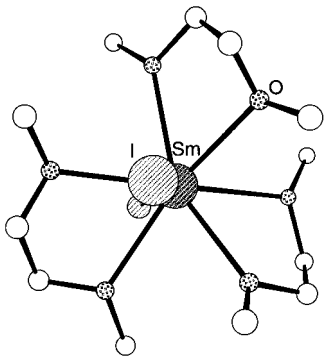
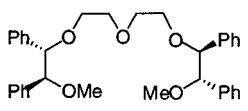


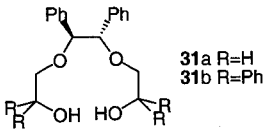
Figure 10. Structure of $\Lambda(\delta\delta\delta)$ -$[SmI_2(dme)_3]$ (dme = $MeOCH_2CH_2OMe$).

lizes as a single enantiomer in a noncentrosymmetric space group.[45] These complexes all racemize rapidly in solution due to the nonrigidity that is inherent in lanthanide chemistry.

The podand ligands **30** and **31**[46] were designed as chiral analogues of tetraglyme and triglyme, which give convenient Lewis acid catalysts when coordinated to $Ln(OTf)_3$.[47]



30



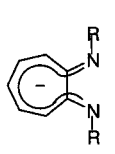
31

Complexes of **30** and **31**a with $Ln(OTf)_3$ have been prepared and characterized crystallographically,[48] and the structures of $[Eu(OTf)_3(\mathbf{30})]$ and $[Yb(OTf)_3(\mathbf{31}a)(H_2O)]$ are shown in Figures 11 and 12. The chelate rings of $[Eu(OTf)_3(\mathbf{30})]$ adopt $\delta\lambda\delta\lambda$ conformations compared with $\lambda\lambda\delta\delta$ for the achiral $[Dy(OTf)_2(tetraglyme)]^+$ analogue.[47] Sm complexes of chiral diols similar to **31** have been used in enantioselective protonatation of enolates (see section X.B).[49]

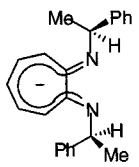
III. Complexes with N-Donor Ligands

A. Anionic N-Donors

Aminotroponiminate ligands **32** have been recognized as alternatives to cyclopentadienyl as supporting ligands for organolanthanide chemistry.[50] $[Y(\mathbf{32})_2N(SiMe_3)_2]$ has been shown to catalyze the hydroamination/cyclization of aminoalkynes,[51] demonstrating the utility of this ligand system in catalytic chemistry. Chiral derivatives are available by incorporation of chiral substituents onto the N atoms as in **33**. To date complex **34** is the only example of a Ln complex with this chiral aminotroponiminate.[52] Homoleptic lanthanide tris(aminotroponiminates) adopt a chiral D_3-symmetric structure (shown by DFT calculations to be the most stable) which undergoes rapid racemization in solution.[53,54]



32



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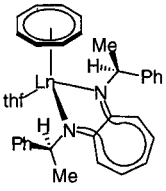


34

Attempts to use the bis(oxazoline) **35** or box ligand in enantioselective lanthanide catalysis have met with a distinct lack of success (see section IX.E), and

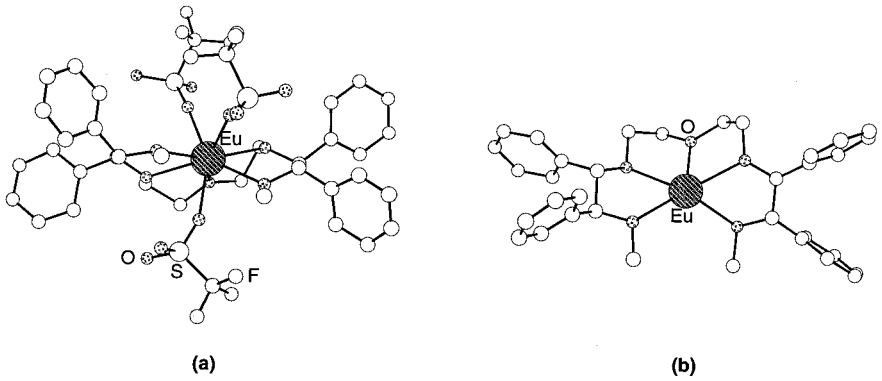


Figure 11. Structure of (a) [Eu(OTf)$_3$(**30**)] and (b) OTf$^-$ ligands removed for clarity.

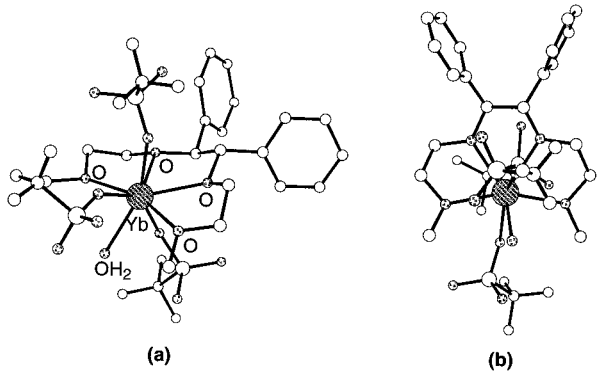
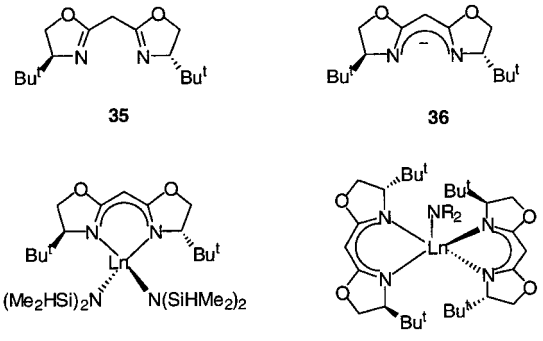


Figure 12. Structure of (a) [Yb(OTf)$_3$(**31**a)(H$_2$O)], and (b) view perpendicular to plane of **31**a ligand.

no lanthanide complexes with this ligand have been isolated. The neutral ligand can be deprotonated to give **36**, and lanthanide complexes **37** and **38** with one or two bis(oxazolinato) ligands have been prepared.[55] It is not possible to prepare [Ln(**36**)$_3$] complexes, presumably for steric reasons.



No catalytic reactions have yet been reported for these complexes. The structure of [Y(**36**){N(SiMe$_2$H)$_2$}$_2$] is shown in Figure 13.

Monomeric Ln complexes with the C_2-symmetric bis(silylamido)biphenyl ligand **39** have been prepared according to reaction 5.[56] Organometallic complexes can be prepared by reaction with LiR, and some catalytic reactions have been reported (see section IX.F).[57] The structure of the chloro complex [Y(**39**)Cl(thf)$_2$] is shown in Figure 14.

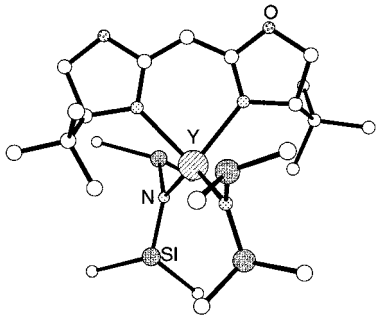


Figure 13. Structure of [Y(**36**){N(SiMe$_2$H)$_2$}$_2$].

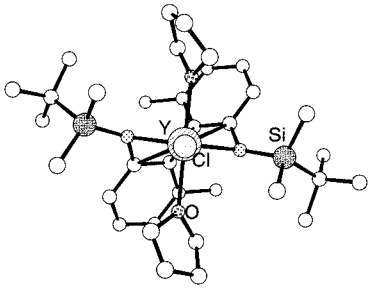
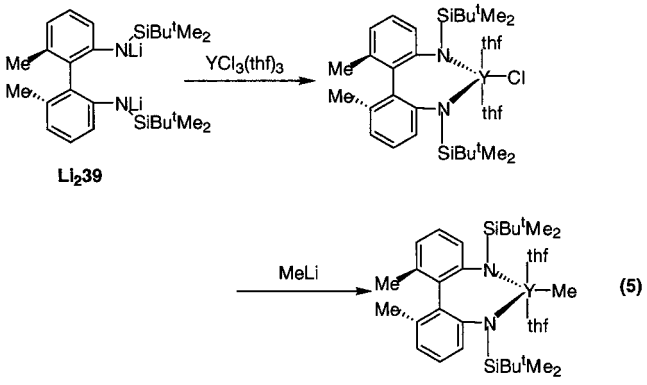
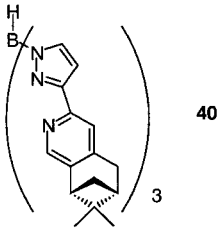


Figure 14. Structure of [Y(**39**)Cl(thf)$_2$].



The C_3-symmetric hexadentate podand ligand **40** is based on a tris(pyrazolylborate) core, with pinene-functionalized pyridine groups. It acts as a hexadentate ligand toward Ln^{3+}, and a Tb complex [TbL(NO$_3$)$_2$] has been prepared and characterized crystallographically. As yet no further investigations of the



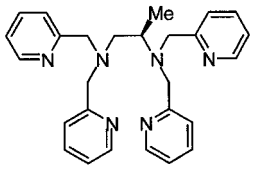
40

complex have been carried out.[58] The structure of [Tb(**40**)$(NO_3)_2$] is shown in Figure 15.

B. Neutral N-Donors

1. Aromatic N-Donors

Aromatic N-donors have been well-known in lanthanide coordination chemistry for decades, and there are several examples of chiral Ln complexes containing pyridine donors. The tetrapyridyl ligand R-tppn **41** forms complexes of reasonable stability in aqueous solution, and the Eu complex has been used as a chiral NMR shift reagent for amino acids (see section VIII).[59] The structure of [Eu(**41**)Cl_2]$^+$ is shown in Figure 16.



41

The coordination chemistry of the achiral tris(2-pyridylmethyl)amine ligand **42** with the lanthanides is well established, and the crystal structure of [LaI_3(**42**)(py)] has been determined.[60] Complexes of the Eu^{3+} and Tb^{3+} with chiral versions of this ligand, **43**, have now been prepared by reaction of $Ln(OTf)_3$ with 3 equiv of ligand in MeCN solution, but these complexes have not been isolated. The luminescence

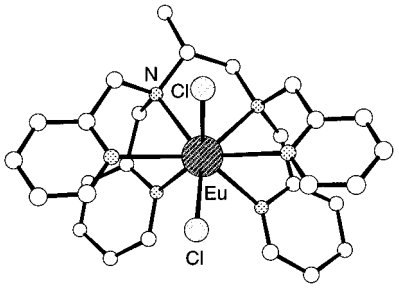
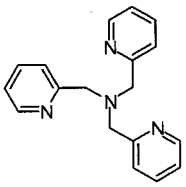


Figure 16. Structure of [Eu(**41**)Cl_2]$^+$.

spectra of the complexes are found to be sensitive to the stereochemistry of the ligand.[61]



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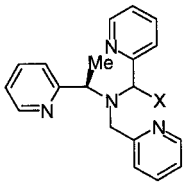
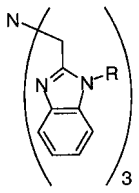


43

X=H; *R*-Me; *S*-Me

The encapsulating benzimidazole ligand **44** forms chiral complexes [Ln(**44**)$_2$]$^{3+}$, and when R = Me, the complex spontaneously resolves to give enantiomerically pure crystals. When R = Pr^i, racemic crystals are formed.[62] Cocrystallization of [Nd(**44**)$_2$]$^{3+}$ with bipy results in formation of a 3-dimensional chiral framework.[63]



44

The sexipyridine ligand **45** gives dinuclear triple helical complexes with transition metals, but with the larger Ln^{3+} it gives a mononuclear complex with a helical (and therefore chiral) arrangement of the

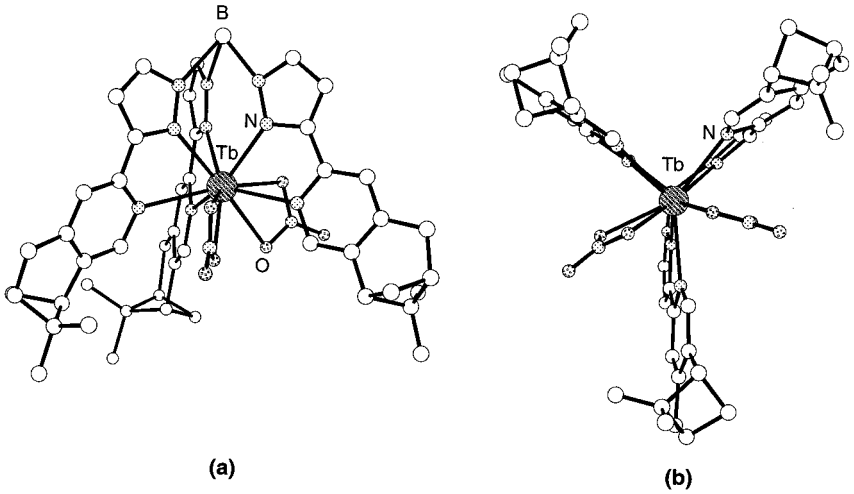


Figure 15. Structure of [Tb(**40**)$(NO_3)_2$]: (a) view perpendicular to the Tb−B axis and (b) view along the Tb−B axis.

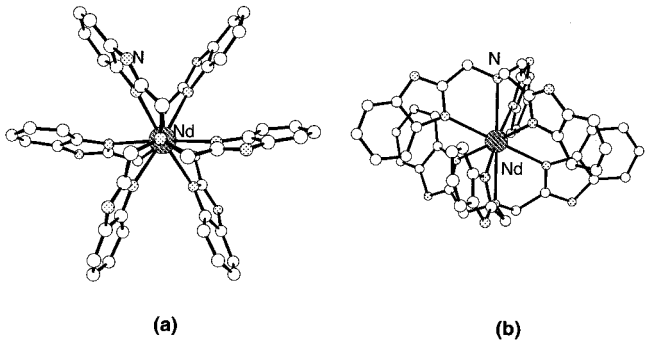


Figure 17. Structure of $[Nd(\mathbf{44})_2]^{3+}$: (a) view along the C_3 axis and (b) view perpendicular to the C_3 axis.

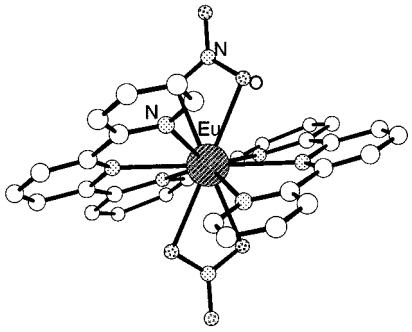
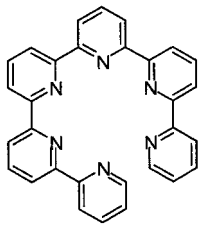


Figure 18. Structure of $[Eu(\mathbf{45})(NO_3)_2]^+$.

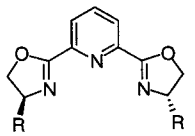
ligand as shown in Figure 18.[64] The complex crystallizes as a racemic mixture.



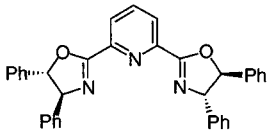
45

2. Pybox Complexes

Pybox ligands **46** with the general structure shown below have been used with great success in enantioselective transition-metal-catalyzed reactions for several years, and the structures of many of the active catalysts have been determined crystallographically.[65]



46



47

The use of pybox ligands in lanthanide chemistry was first reported in 1997 when catalysts derived from $Ln(OTf)_3$ and Pr^i-pybox were used for enantioselective 1,3-dipolar cycloaddition reactions.[66] Since then other rare-earth pybox catalysts have been reported, and these will be discussed in more detail in section IX.E.[67−71]

NMR studies have shown that reaction of $LnCl_3$ with 1 equiv of pybox under rigorously anhydrous conditions leads to selective formation of $[LnCl_3(pybox)_2]$ as a 1:1 mixture with unreacted $LnCl_3$. There is as yet no crystallographic characterization of $[LnCl_3(pybox)_2]$ complexes, but a preliminary report of the crystal structure of $[La(OTf)_3(Pr^i\text{-pybox})_2]$ has been published;[72] this structure is shown in Figure 19. Pybox generally acts as a tridentate ligand in transition-metal chemistry, with N−M−N bond angles close to 90°; however, the larger Ln^{3+} ions are unable to adopt this geometry, and N−La−N angles of approximately 60° are found, with the La and donor N atoms being coplanar. The dihedral angle between the planes of the two pybox ligands is approximately 77°, and the two pybox ligands together cooperate to form a chiral binding site at Ln. Inspection of a La(Pr^i-pybox) fragment as shown in Figure 19 suggests that a single pybox ligand is unlikely to achieve this in cases where the substrate is monodentate.

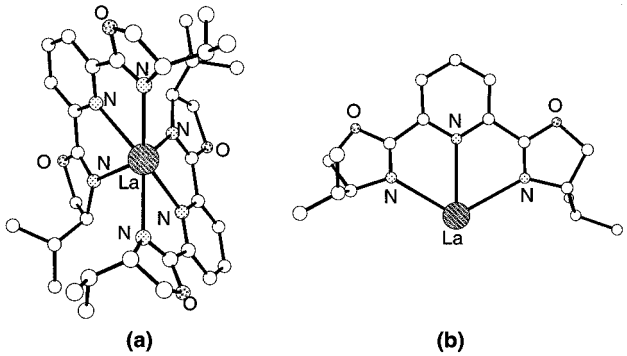


Figure 19. Structure of $[La(OTf)_3(S\text{-}Pr^i\text{-pybox})_2]$ (OTf^- omitted for clarity): (a) view showing the two pybox ligands and (b) view of a La(*S*-Pr^i-pybox) fragment.

Size effects in these lanthanide bis(pybox) complexes are apparent on traversing the lanthanide series: the solubility properties of $[Yb(OTf)_3(Pr^i\text{-pybox})_2]$ are somewhat different from those of the La complex, and a crystal structure determination has revealed this complex to be $[Yb(OTf)_2(Pr^i\text{-pybox})_2][OTf]$.[73] The Yb^{3+} ion is clearly not large enough to accommodate three coordinated OTf^- groups as well as two tridentate pybox ligands. It is perhaps worth noting that pybox does not always act as a tridentate ligand in transition-metal chemistry.[74,75] Reaction of $Ln(OTf)_3$ with racemic Pr^i-pybox has also been investigated. The outcome of the reaction varies with the ionic radius of Ln: reaction of *rac*-Pr^i-pybox with $Eu(OTf)_3$ gives exclusively $[Eu(OTf)_3(RR\text{-}Pr^i\text{-pybox})(SS\text{-}Pr^i\text{-pybox})]$, whereas $Yb(OTf)_3$ gives a mixture of mainly *RR*- and *SS*-$[Yb(OTf)_2(Pr^i\text{-pybox})_2)][OTf]$, along with a very small amount of $[Yb(OTf)_2(R\text{-}Pr^i\text{-pybox})(S\text{-}Pr^i\text{-pybox})][OTf]$.[73] Investigations of Co(II) bis(pybox) complexes have shown that steric effects result in preferential formation of heterochiral complexes with racemic pybox,[76] and so it is perhaps surprising that $Yb(OTf)_3$ gives mainly homochiral bis(pybox) complex. The structure of $[Eu(R\text{-}Pr^i\text{-pybox})(S\text{-}Pr^i\text{-pybox})]$ is shown in Figure 20.

The tetraphenyl pybox ligand **47** forms a mono(pybox) complex $[La(OTf)_2(\mathbf{47})(H_2O)_4][OTf]$, which is an effective catalyst for enantioselective Mukaiyama−Michael reaction and has been characterized crystallographically.[70] This nine-coordinate complex is

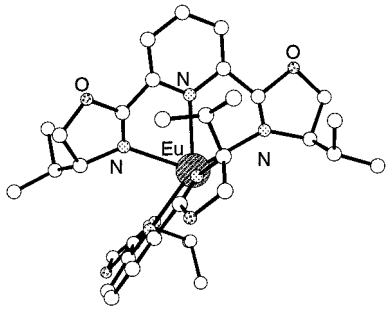


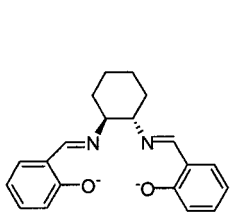
Figure 20. Structure of [Eu(OTf)$_3$(*S*-Pr^i-pybox)(*R*-Pr^i-pybox)] (OTf$^-$ omitted for clarity).

prepared by the reaction of La(OTf)$_3$ with 1 equiv of **47** in MeCN without any precautions to exclude moisture. Two views of the structure are shown in Figure 21. The bond distances and angles in the La(pybox) fragment of this complex are very close to those of [La(OTf)$_3$(Pr^i-pybox)$_2$]. One other rare-earth triflate mono(pybox) complex has been characterized crystallographically: [Sc(OTf)$_3$(Ph-pybox)(H$_2$O)] is prepared by reaction of Sc(OTf)$_3$ with 1 equiv of Ph-pybox in CH_2Cl_2, and the structure of this seven-coordinate complex is shown in Figure 22.[71] As expected for the smaller metal ion, the N−M−N angles have increased to ca. 68° in the Sc pybox fragment compared with ca. 60° in the La pybox complexes.

IV. Complexes with Mixed O/N-Donors

A. Acyclic Schiff Base Complexes

Liu studied reactions of the salicylaldehyde Schiff base **48** with organolanthanide complexes. Heteroleptic complexes with cyclopentadienyl and salen-type ligands **48** have been reported for Yb[77] and Sm.[78,79] The products of these reactions are dimeric with the general structure **49**; however, the complexes have not been not isolated enantiomerically pure.



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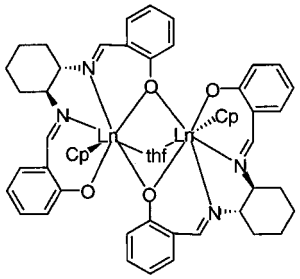
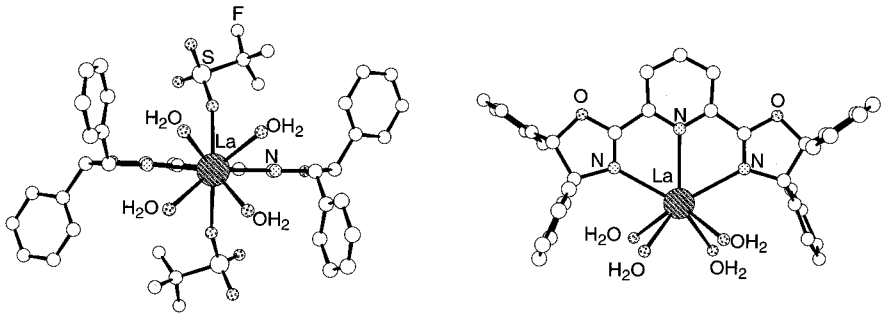


49

Reaction of Cp$_3$Sm with *S*-*N*-1-phenylethylsalicylaldimine **(50)** results in intramolecular H-transfer and C−C bond formation to give complex **51**.[79]

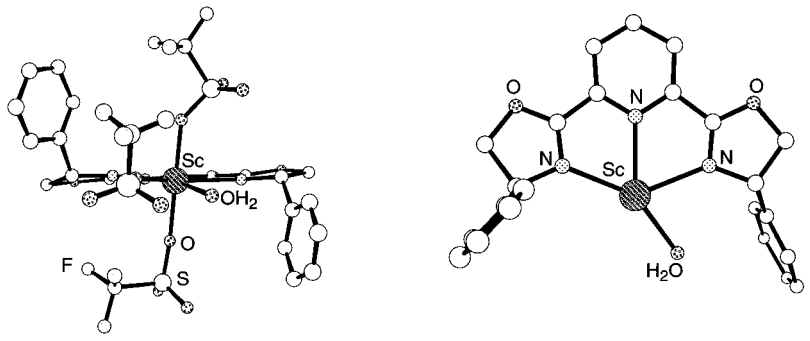
B. Aminocarboxylate Complexes

Achiral multidentate aminocarboxylate ligands can potentially adopt several chiral conformations in



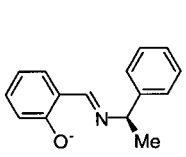
(a) **(b)**

Figure 21. Structure of [La(OTf)$_2$(**47**)(H$_2$O)$_4$]$^+$: (a) view parallel to **47** and (b) view perpendicular to plane of **47** (OTf$^-$) omitted for clarity.



(a) **(b)**

Figure 22. Structure of [Sc(OTf)$_3$(Ph-pybox)(H$_2$O)]: (a) view parallel to pybox and (b) view perpendicular to plane of pybox (OTf$^-$) omitted for clarity.



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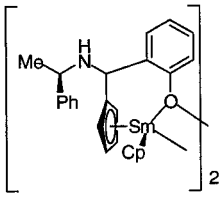
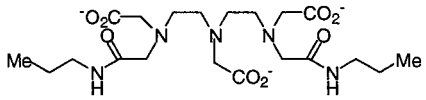


51

solution due to the formation of chelate rings. For example, Ln complexes with ligand **52** can exist as four diastereomeric pairs of isomers, and the dynamics of these complexes have been investigated by NMR spectroscopy.[80] The introduction of a chiral center can lock the structure into a favored conformation and hence simplify solution behavior. This has been investigated with Y complexes of the chiral ligand **53**, which exist as a single isomer in solution.[81]



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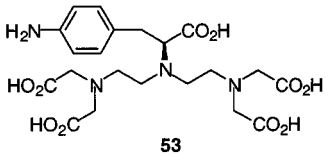
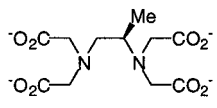


53

One of the main interests in chiral aminocarboxylate complexes has been their application as chiral shift reagents for use in aqueous solution, a subject that will be discussed in section VIII. Complexes of the chiral EDTA analogue **54** have proved very effective, but as yet there is no report of crystallographic characterization.

The Eu complex of the *trans*-diaminocyclohexane-derived aminocarboxylate **55** has been prepared from racemic ligand.[82] It crystallizes as a heterochiral H_2O-bridged dimer, the structure of which is shown in Figure 23.



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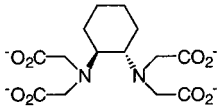


55

C. Tris(dipicolinate) Complexes

The tridentate dipicolinate (DPA) ligand **56** forms stable nine-coordinate complexes $[Ln(DPA)_3]^{3-}$ **(57)** with all the lanthanide elements. When the counterion is achiral (e.g., Na^+), these complexes crystallize in centrosymmetric space groups with both Δ and Λ forms present in the crystal. The structure of the Δ enantiomer of $[Tb(DPA)_3]^{3-}$ is shown in Figure 24. A chiral counterion such as $[Co(sar)]^{3+}$ **(58)** can result in a single enantiomer of $[Ln(DPA)_3]^{3-}$ in the crystal; this has been observed in the structure of Λ-[Eu-$(DPA)_3$]Δ-[Co(sar)].[83] The enantiomers interconvert

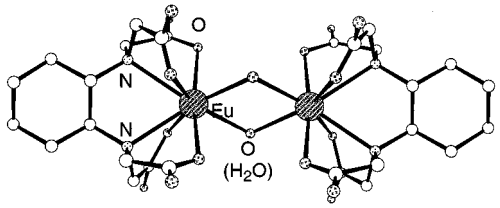
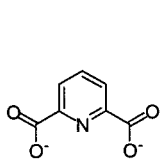


Figure 23. Structure of $[Eu(\mathbf{55})(H_2O)]_2^{2-}$.

rapidly in solution: the rate of enantiomerization is ca. 10 s^{-1} as measured spectroscopically for [Eu-$(DPA)_3]^{3-}$.[84]



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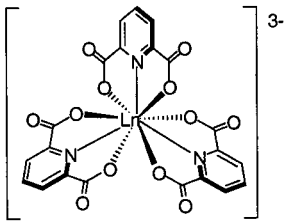

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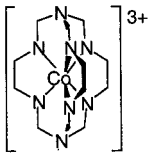
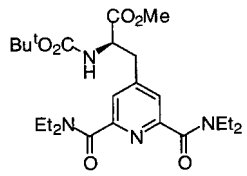


58

A chiral substituent has been incorporated into the neutral dipicolinamide ligand **59**, which forms nine-coordinate complexes $[Ln(\mathbf{59})_3]^{3+}$. Like $[Ln(DPA)_3]^{3-}$ the complexes of **59** undergo rapid exchange of diastereomers in solution and it is impossible to isolate a single diastereomer.[85]



59

The tris(dipicolinate) complexes **57** with Eu^{3+} and Tb^{3+} are strongly luminescent, with luminescent lifetimes in the order of milliseconds, and their luminescence and circularly polarized luminescence (CPL)[86] have been the subject of many detailed investigations. Most of these investigations have been directed toward understanding enantioselective

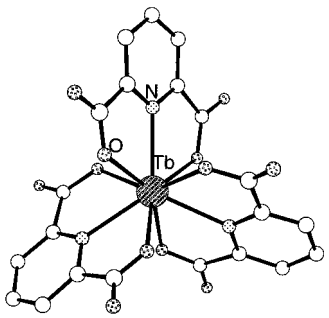


Figure 24. Structure of Δ-$[Tb(DPA)_3]^{3-}$.

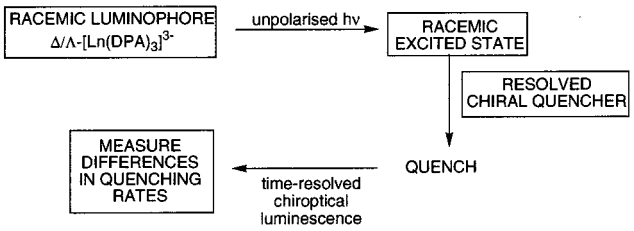
quenching processes. In these experiments, an enantiomerically pure quencher is used to investigate the effect on CPL. The first chiral quencher to be investigated was resolved $[Ru(phen)_3]^{2+}$.[87] In eqs 6 and 7 Δ^*/Λ^* represent the electronically excited enantiomers of $[Ln(DPA)_3]^{3-}$ and (R−Q) represents the resolved quencher. The interaction between racemic donor and enantiomerically pure quencher gives diastereomeric pairs, which may differ both in formation constant and in energy transfer rates within the pairs. Both these mechanisms can give rise to chiral discrimination, resulting in selective quenching of one excited-state enantiomer.

$$\Delta^* + (R - Q) \rightarrow [\Delta^* \cdot (R - Q)] \rightarrow \Delta + (R - Q)^* \quad (6)$$

$$\Lambda^* + (R - Q) \rightarrow [\Lambda^* \cdot (R - Q)] \rightarrow \Lambda + (R - Q)^* \quad (7)$$

The general scheme of the experiment is shown in Scheme 1.

Scheme 1



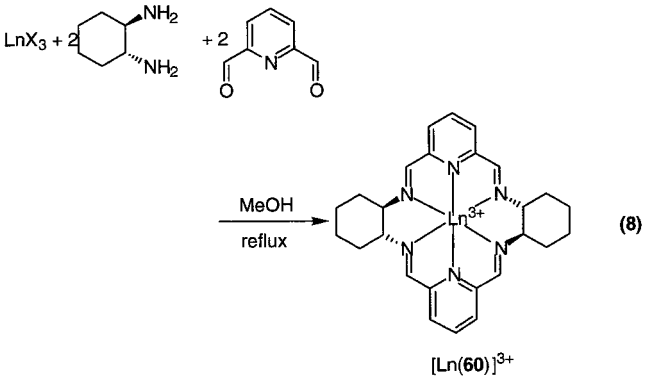
Further studies of the $[Tb(DPA)_3]^{3-}/[Ru(phen)_3]^{2+}$ system have shown that tight ion pair formation is important in the energy transfer process and that the fastest quenching occurs in the lowest ionic strength solutions.[88] The relative rates of homochiral ($\Delta\Delta$ or $\Lambda\Lambda$) and heterochiral ($\Delta\Lambda$ or $\Lambda\Delta$) quenching were found to differ with solvent. In MeOH or MeOD, heterochiral quenching was found to be most efficient, and in H_2O or D_2O, homochiral quenching was the faster process.[89,90] A thermodynamic study of this solvent dependence concluded that enthalpy effects favor homochiral vs heterochiral quenching and that entropy effects favor heterochiral vs homochiral quenching; enthalpy effects dominate in H_2O, and entropy effects dominate in MeOH.[91] Enantioselective quenching of $[Ln(DPA)_3]^{3-}$ by several other enantiomerically pure transition-metal complexes has also been investigated. These include $[Co(en)_3]^{3+}$ and Co^{3+} complexes with *trans*-1,2-diaminocyclohexane[92,93] and a Cu(I) 'trefoil-knot'.[94]

All of the enantioselective quenching processes described above involve chiral recognition, and there is growing interest in studying biomolecules. Detailed studies of the enantioselective quenching of $[Ln(DPA)_3]^{3-}$ luminescence by vitamin B_{12} have shown that formation of the encounter complex between the donor and acceptor is the most important contribution to the quenching.[95] NMR studies suggest that the Λ-$[Ln(DPA)_3]^{3-}$−vitamin B_{12} complex is the more stable diastereomer and that the interaction is via H-bonding between the carboxylate oxygens of the DPA ligands and the amide hydrogens of the corrinoid.[96] Quenching by cytochromes[97,98] and by Co nucleotides[99] has also been investigated. In the case of the metalloproteins, there is some chiral discrimination in the energy transfer process.

V. Complexes with Macrocyclic Ligands

A. Schiff Base Macrocycles

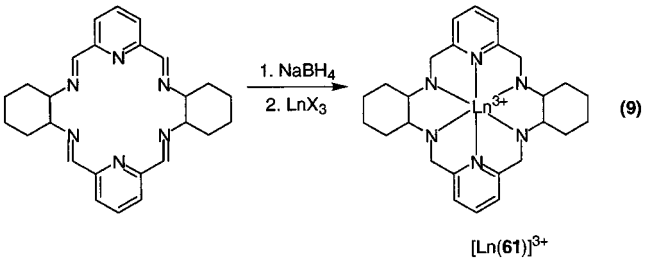
Schiff base macrocycles are well-known in lanthanide chemistry,[100] and a wide range of complexes are easily prepared by template condensation reactions between diamines and dicarbonyl compounds as shown in reaction 8. Several chiral diamines are commercially available in enantiomerically pure form, and this gives a ready route to chiral macrocyclic ligands. However, there are few characterized examples of lanthanide complexes of this type.



(8)

The condensation reaction of enantiomerically pure *trans*-diaminocyclohexane with 2,6-diformylpyridine in the presence of lanthanide salts was first reported in 1992.[101] The complexes of ligand **60**, which show moderate stability in aqueous solution, were characterized by NMR and luminescence spectroscopy but not by X-ray diffraction. X-ray quality crystals were obtained from a reaction using racemic diamine. Fortunately, despite the potential for formation of mixtures of diastereomers, the diastereomerically pure pair of enantiomers (*RRRR* and *SSSS*) is formed.[102] The enantiomerically pure complexes prepared from *RR-trans*-diaminocyclohexane for Ln = Nd or Tm and X = NO_3 have been characterized by X-ray diffraction[103] and NMR spectroscopy.[104] The structure of *RRRR*-$[Nd(\mathbf{60})(NO_3)_2]^+$ is shown in Figure 25.

Reduction of the tetraimine macrocycle with borohydride yields complexes $[Ln(\mathbf{61})]^{3+}$ of the more flexible tetraamine macrocycle as shown in reaction 9.



(9)

The La complex with racemic ligand **61** has been characterized crystallographically,[105] and the structure is shown in Figure 26.

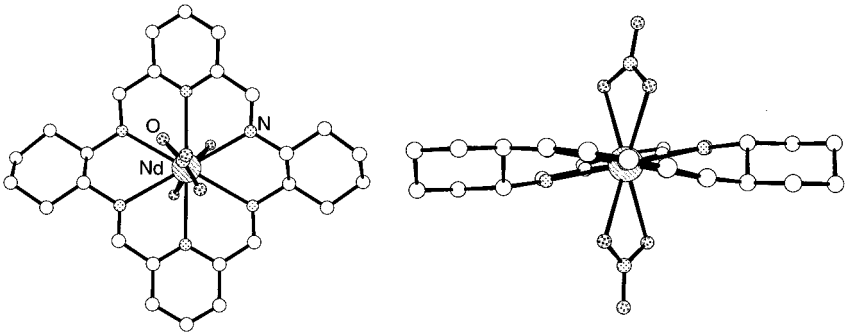
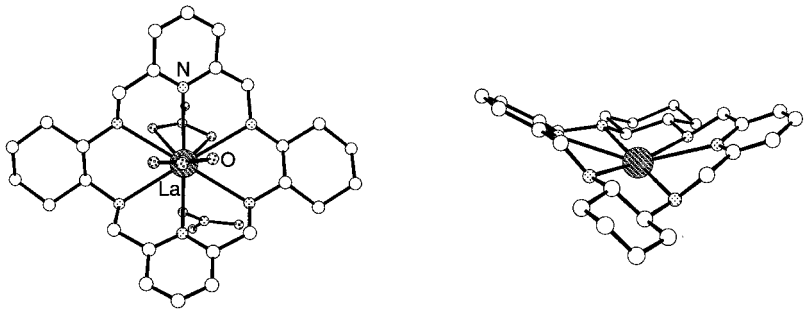
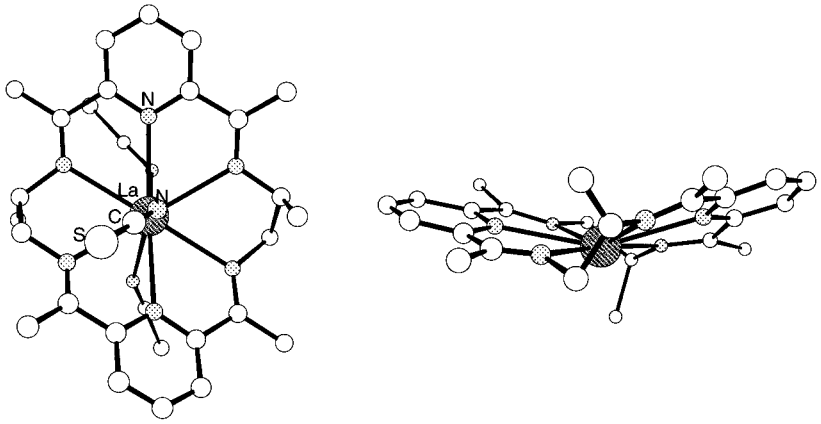


Figure 25. Structure of *RRRR*-[Nd(**60**)$(NO_3)_2$]$^+$.



(a) (b)

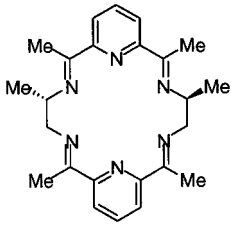
Figure 26. Structure of [La(**61**)$(NO_3)_3$]: (a) perpendicular to the macrocycle and (b) showing the twist of the macrocycle (NO_3^- omitted for clarity).



(a) (b)

Figure 27. Structure of [La$(NCS)_3$(**62**)]: (a) perpendicular to the macrocycle and (b) showing the twist of the macrocycle (NCS^- omitted for clarity).

The complex [La$(NCS)_3$(**62**)] with an unsymmetrically dimethyl-substituted ligand has been characterized crystallographically, and the structure is shown in Figure 27.[106]



62

B. Mixed O,N-Donor Macrocycle

Kobayashi recently reported the use of the hybrid O,N-donor macrocyclic ligand **63** in enantioselective catalysis by early Ln$(OTf)_3$ (see section IX.E). The crystal structure of [Pr(**63**)$(NO_3)_2$][NO_3] has been determined and is shown in Figure 28.[107]

C. Metallacrown Macrocycles

Chiral amino hydroxamic acids undergo a template condensation reaction in the presence of Cu^{2+} and Ln^{3+} to give a metalla-15-crown-5 macrocycle complex **64** as shown in reaction 10. In complex **64**, which

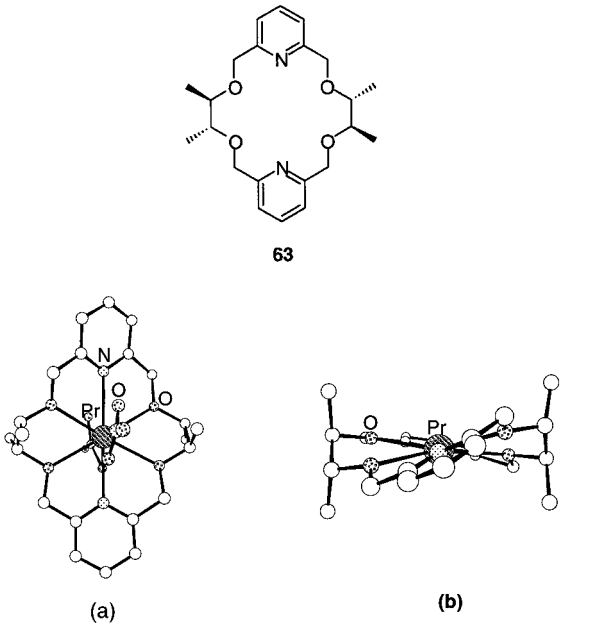
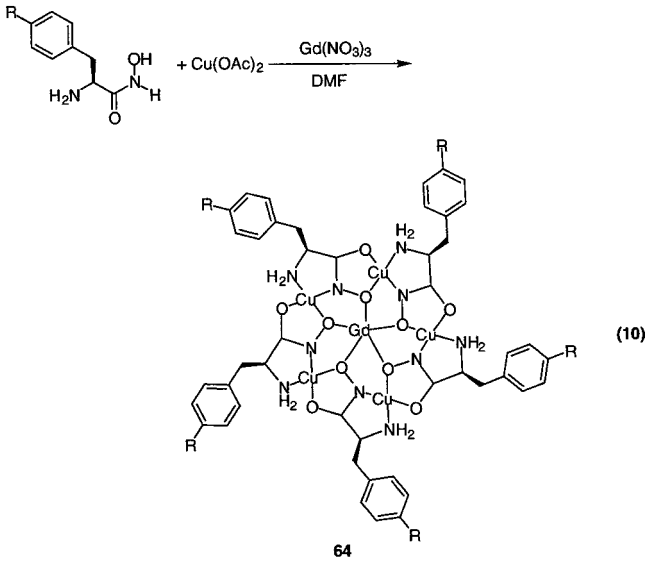


Figure 28. Structure of [Pr(**63**)$(NO_3)_2$][NO_3]: (a) perpendicular to the macrocycle and (b) view along the N−Pr−N direction showing the twist of the macrocycle (NO_3^- omitted for clarity).

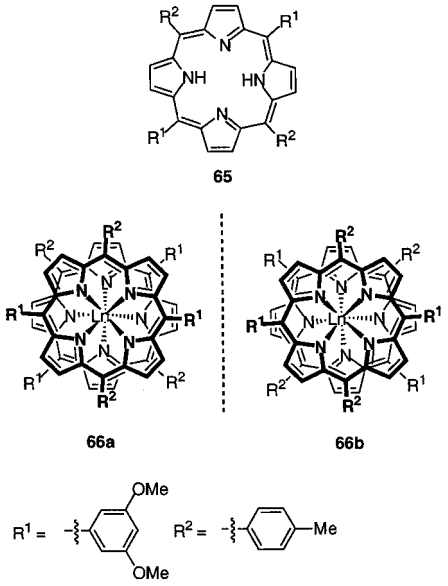
is remarkably stable in aqueous solution, the Ln^{3+} is encapsulated in the plane of the five O-donors.[108]



When R = OH (tyrosine hydroxamic acid), the macrocycle complexes associate in solution to form dimers where four phenol groups from each macrocycle extend out into the solution and one phenol group bends across to bind to a Cu atom of the other macrocycle. The cavity thus formed between the two macrocycles can selectively bind NO_3^-, excluding Cl^- or OAc^-.[109] As yet there is no report of selective binding of chiral anions by this chiral cavity.

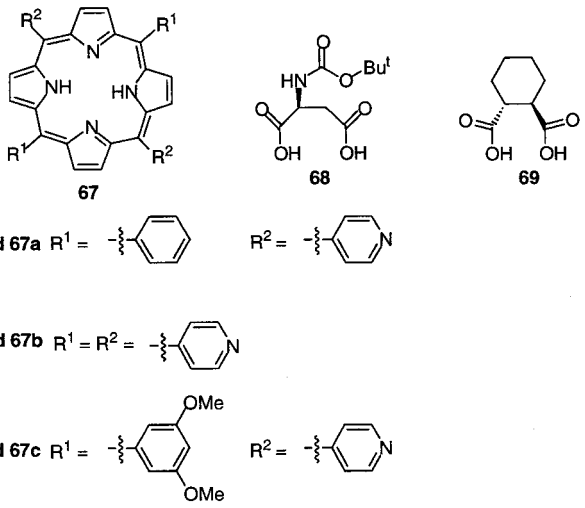
D. Double-Decker Porphyrins

The reaction of [Ce(acac)$_3$] with octaethylporphyrin H_2OEP to give double-decker complexes [Ce(OEP)$_2$] was reported in 1986. The double-decker Ce(IV) complexes are soluble in hydrocarbons and can be purified by chromatography.[110] Free rotation of the porphyrin rings occurs in solution unless this process is hindered by the presence of sterically demanding substituents on the ring as in **65**. If $R^1 \neq R^2$ and rotation is hindered, then the complex can in principle exist as two enantiomeric rotamers **66a** and **66b** with D_2 symmetry.



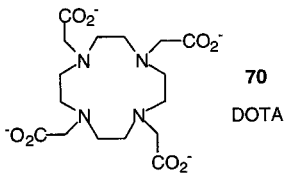
When R^1 = 3,5-dimethoxyphenyl and R^2 = *p*-tolyl, the ring rotation is slowed sufficiently for the enantiomers to be separated by chiral HPLC.[111] There is no rotation on the NMR time scale up to 110°C, although there is slow racemization in solution by ring rotation. No ligand exchange is observed. Reduction of the Ce(IV) to Ce(III) increases the rate of racemization by a factor of ≈300,[112] and La(III) complexes show much faster ring rotation than Ce(IV) complexes.[113] Use of a 'strapped' porphyrin ligand where the two porphyrin rings are linked by a polyether chain also allows separation of enantiomers by chiral HPLC.[114]

The chirality of the rotamers of Ce bis(porphyrin) complexes has been exploited in molecular recognition of chiral dicarboxylic acids. When the porphyrin bears a pyridine substituent as in **67a** and **67b**, H-bonding interactions between the pyridine N atoms and the carboxylic acid groups can occur. With a dicarboxylic acid, this interaction can lock the top and bottom porphyrin rings, thus preventing ring rotation. A positive allosteric effect is observed because once the first dicarboxylic acid is bound, the rotation of the porphyrin rings is suppressed and binding of subsequent guests is enhanced. This interaction is optimized for acids where the carboxylate groups are separated by a C_2 spacer such as **68** or **69**.[115] The Ce(IV) complex with ligand **67c** shows restricted rotation of the porphyrin rings, and chiral dicarboxylic acid guests can bind and lock the rings into a single enantiomeric form, which racemizes only very slowly on decomplexation of the guests by addition of an excess of pyridine. This has been suggested as prototype for a molecular memory.[116]



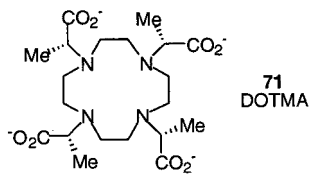
E. DOTA and Related Ligands

Complexes with the DOTA ligand **70** are among the most stable complexes of the lanthanides in aqueous solution and because of this great stability have attracted much interest, e.g., as contrast agents for magnetic resonance imaging.

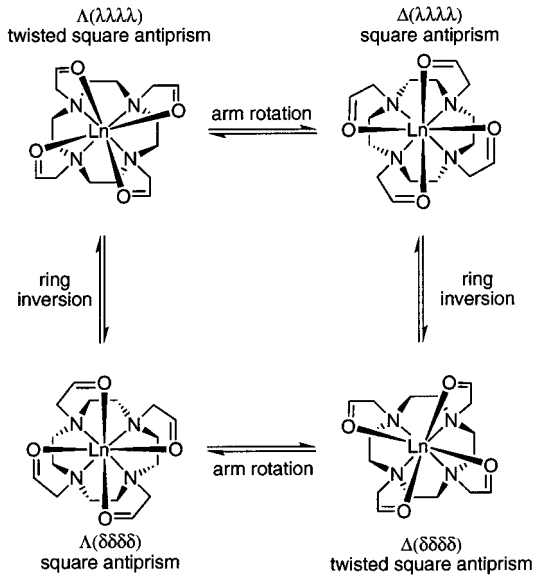


There are two sources of chirality in DOTA complexes: conformational chirality in the $LnNC_2N$ chelate rings and helical chirality arising from the orientation of the pendant acetate arms. Ln DOTA complexes can exist in two diastereomeric forms: $\Delta(\lambda\lambda\lambda\lambda)/\Lambda(\delta\delta\delta\delta)$ and $\Delta(\delta\delta\delta\delta)/\Lambda(\lambda\lambda\lambda\lambda)$, which are illustrated in Scheme 2. The complexes crystallize in centrosymmetric space groups with both enantiomers present; they have C_4 symmetry and contain an axially coordinated H_2O molecule. Both diastereomeric forms are observed in solution with their relative ratios determined by the radius of Ln^{3+}. These structures and their isomerization processes have been studied in detail by NMR spectroscopy for DOTA complexes[117,118] and related structures with amide[119] and hydroxyethyl pendant arms.[120]

The helical chirality can be locked by introduction of chiral pendant arms. For example, the Me-substituted ligand *R*-DOTMA **(71)** gives exclusively Λ helical chirality; the Yb complex exists in two diastereomeric forms in solution: $\Lambda(\lambda\lambda\lambda\lambda)$ (major) and $\Lambda(\delta\delta\delta\delta)$ (minor).[121] The near-IR circular dichroism spectrum of $[Yb(DOTMA)]^{3+}$ shows several features around 980 cm^{-1} (Yb f−f transitions) with very high disymmetry factors.[122]



Scheme 2



Chiral amide ligands **72** (Figure 29) give a single stereoisomer with Ln, and the crystal structures of Eu complexes with both enantiomers of the ligand have been determined. As shown in Figure 29, the *SSSS*-ligand gives the $\Delta(\lambda\lambda\lambda\lambda)$ complex and the *RRRR*-ligand gives the $\Lambda(\delta\delta\delta\delta)$ complex.[123,124] These complexes are stereochemically rigid, and there is no Δ/Λ interconversion in the temperature range 220−320 K. The Tb complex is highly emissive due to energy transfer from the pendant arm aryl groups, and all the complexes exhibit strong circularly polarized luminescence. These complexes and analogues with different aryl substituents on the pendant arms have been studied in detail by circularly polarized luminescence spectroscopy.[123,125,126]

The amino acid complex **73** adopts a square antiprismatic structure in aqueous solution; however, in the presence of hydrogencarbonate, HCO_3^- occupies the axial site and the new complex adopts a twisted square antiprismatic structure **74** as shown in Scheme 3.[127] This structural change leads to changes in the circularly polarized luminescence and thus to the possibility of sensing oxyanions such as HCO_3^- and HPO_4^{2-}.[128,129]

The incorporation of hydroxypropyl pendant arms into the macrocycle as in THP (**75**) also imparts stereochemical rigidity to the complexes, and only one diastereomer is observed in solution. Unfortunately no complexes with the homochiral ligand have been characterized crystallographically: the crystal structure reported is of a mixture of four stereoisomers prepared from *RRRS*- and *SSSR*-ligand.[130] NMR studies have shown that there is an ion-pairing interaction between diamagnetic [La(*SSSS*-THP)]$^{3+}$ and paramagnetic $[Tb(DOTP)]^-$ (DOTP = **76**), which exists as a mixture of rapidly interconverting enantiomers. The interaction results in chiral resolution in the NMR spectrum. Chiral resolution is also observed on addition of the chiral base *N*-methyl-D-(−)-glucamine **77** to $[Eu(DOTP]^-$.[131] In this case the

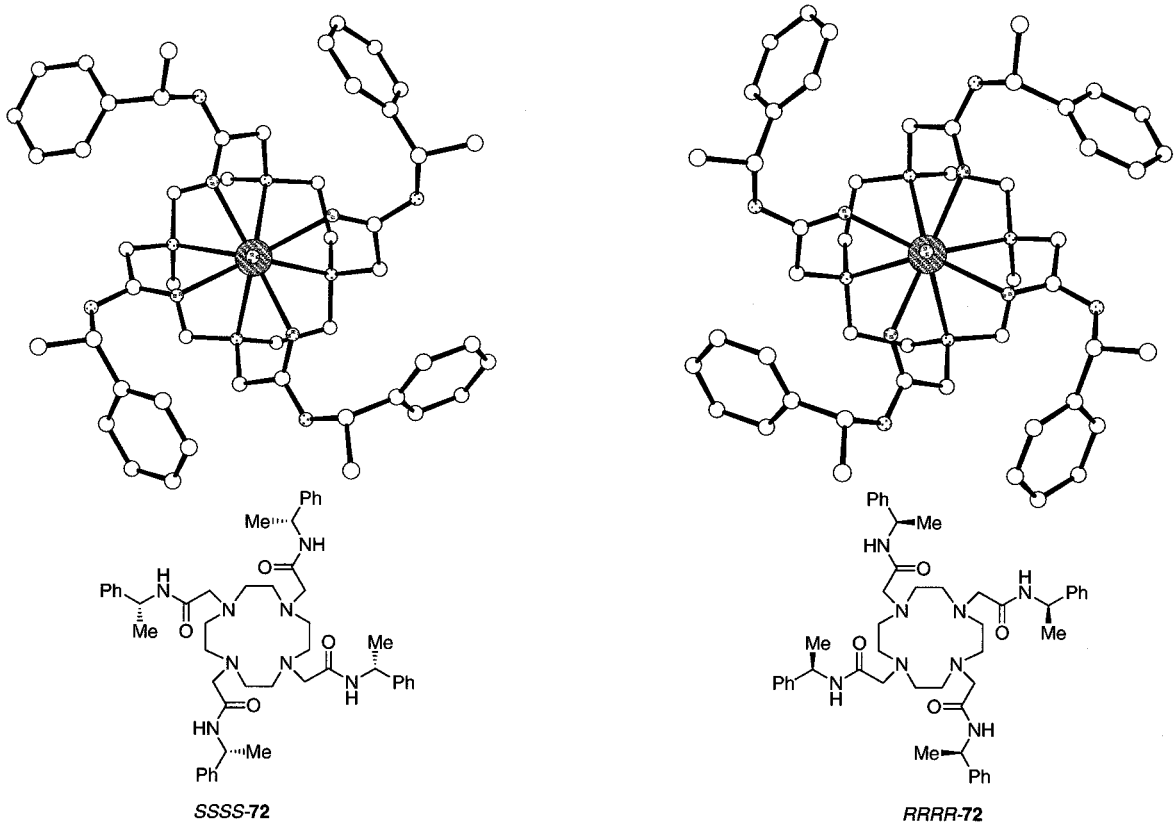
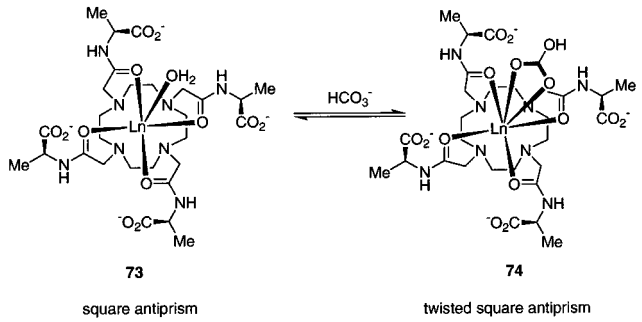
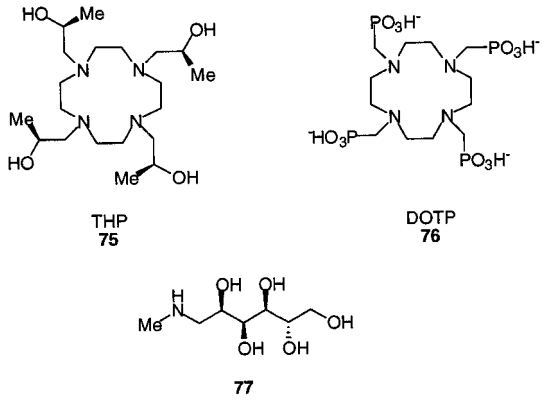


Figure 29. Structures of the $\Delta(\lambda\lambda\lambda\lambda)$ and $\Lambda(\delta\delta\delta\delta)$ enantiomers of $[Eu(\mathbf{72})(H_2O)]^{3+}$.

Scheme 3

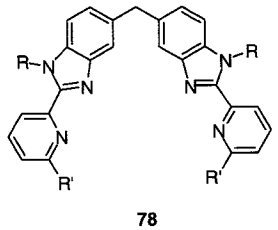


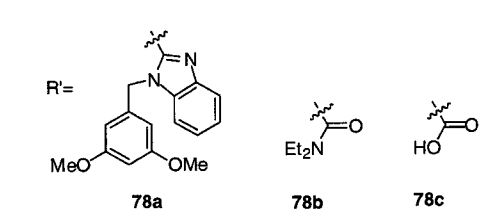
enantiomer ratio is found to be dependent on pH, temperature, and the amount of added base.



VI. Helicate Complexes

The structures of helicate complexes are intrinsically chiral, and although virtually all of these complexes were prepared as racemic mixtures using achiral ligands, a review of chiral lanthanide complexes would not be complete without at least a brief allusion to this fascinating area of coordination chemistry. Ligand **78** is designed to act as a bis(terdentate) ligand for the large Ln^{3+} ions, and the requirement of Ln^{3+} for a high coordination number, combined with weak stacking interactions between the ligands, results in self-assembly of $[Ln_2(\mathbf{78})_3]^{6+}$ dinuclear triple helices.





These have been prepared for **78a**,[132] **78b**,[133] and **78c**,[134,135] which all crystallize as racemates, and the structure of $[Eu_2(\mathbf{78a})_3]^{6+}$ is shown in Figure 30. The self-assembly of these helicates as well as mixed lanthanide−transition-metal complexes has been reviewed.[136,137]

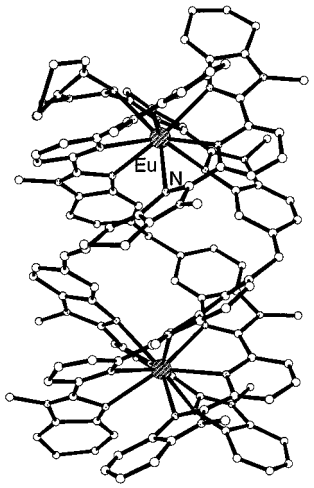
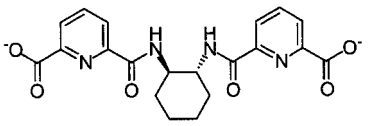


Figure 30. Structure of the helicate $[Eu_2(\mathbf{78a})_3]^{6+}$.

Enantiomerically pure helicate complexes have been prepared in aqueous solution using ligand **79**, which consists of two dipicolinic acid moieties linked by a chiral cyclohexane diamine unit. Neutral complexes $[Ln_2(\mathbf{79})_3]$ self-assemble on reaction of $H_2\mathbf{79}$ with $LnCl_3$ These complexes have high stability (log $K = 31.6$), and luminescence spectroscopy shows that H_2O is excluded from the primary coordination sphere. Luminescence spectroscopy also shows that, as expected, they adopt a D_3-symmetric structure.[138]



79

VII. Complexes with Cyclopentadienyl or Indenyl Ligands

Organolanthanide complexes with cyclopentadienyl ancillary ligands are very effective catalysts for numerous alkene transformations, and so there has been considerable effort directed toward synthesis of chiral analogues of these catalysts. The cyclopentadienyl ligand set is attractive for catalytic lanthanide complexes because its steric effects can be tailored to meet the requirements of the large lanthanide ions.

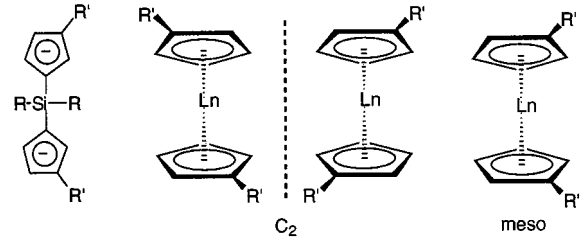
A. Bis(cyclopentadienyl) Complexes

Metallocene catalysts are well established in transition-metal chemistry, and the most effective enantioselective catalysts in this class are based on C_2-symmetric structures, often containing linked Cp or indenyl rings. Bis(cyclopentadienyl) complexes also constitute by far the most important class of chiral lanthanide cyclopentadienyls. Representative examples will be dealt with in this section; a summary of known complexes is given in Table 1 (complexes isolated as racemic mixtures) and Table 2 (complexes isolated enantiomerically pure).

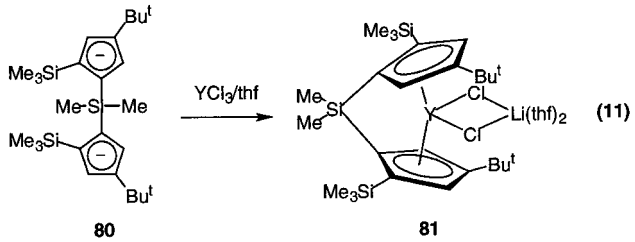
Some general approaches to the synthesis of C_2 symmetric complexes are as follows: Substituted Cp or indenyl rings linked, e.g., by CR_2 or SiR_2; donor-functionalized Cp or indenyl; Cp or indenyl rings linked by a donor-functionalized linker.

B. Linked Cyclopentadienyl or Indenyl Ligands

The use of linked substituted Cp ligands can give both the C_2-symmetric and the *meso* diastereomers as shown below.



A suitable choice of substituents on the ring can favor formation of one diastereomer, although steric influences of ligands are significantly less effective for the large Ln ions than in transition-metal chemistry. However, the linked disubstituted ligand **80** gives exclusively the C_2-symmetric diastereomer **81** with Y as shown in reaction 11.[139]



80 **81**

In this case the exclusive formation of the C_2-symmetric diastereomer avoids unfavorable Me_3Si-Me_3Si interactions. The structure of complex **81** is shown in Figure 31.

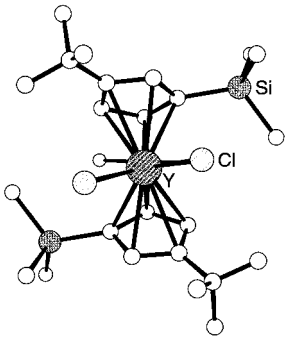


Figure 31. Structure of complex **81** ($Li(thf)_2$ fragment omitted for clarity).

Me_2Si-linked bis(indenyl) ligands have also been used to prepare exclusively C_2-symmetric structures which were the first rare-earth analogues of Brintzinger-type metallocenes.[140] Bis(indene) **82** reacts with a lanthanide tris(silylamide) complex to give a heteroleptic C_2-symmetric complex **83** as shown in reaction 12. The crystal structure of complex **83** is shown in Figure 32.

The use of an ether linkage to join indenyl groups has been effective in favoring formation of C_2-symmetric complexes, and with ligand **84** complex **85** is

Table 1. Chiral Lanthanide Bis(cyclopentadienyl) or -(indenyl) Complexes Isolated as Racemates

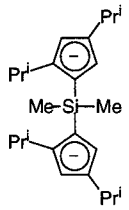
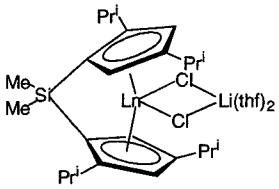
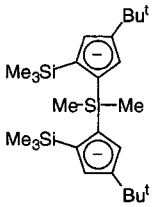
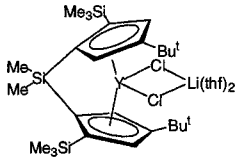
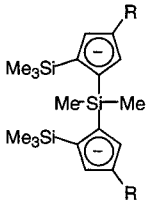
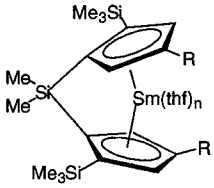
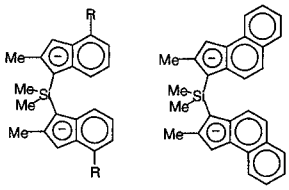
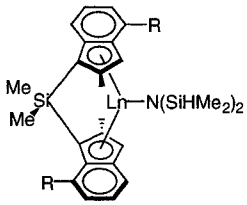
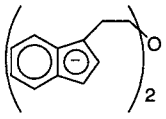
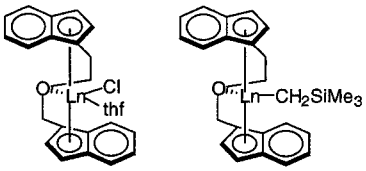
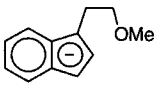
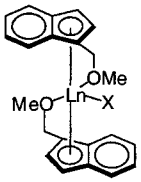
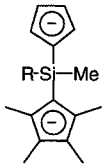
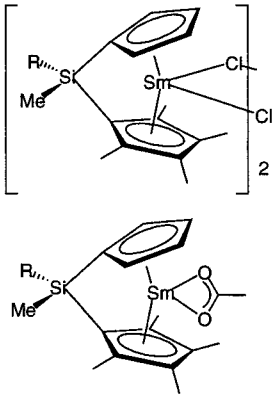
Entry	Ligand	Complex	Ref
1			240
2			139
3	 R=Bu^t or Bu^{t}Me$_2$Si	 R=Bu^t n=2 R=Bu^{t}Me$_2$Si n=3	225
4	 R=H or Ph		140,241
5			141,242
6		 X=Cl or μ_2-H_2BH_2	146,243
7			144

Table 1. (Continued)

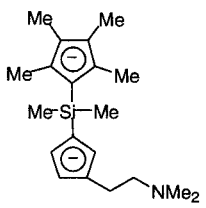
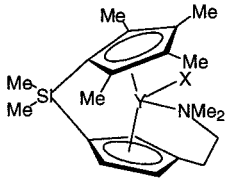
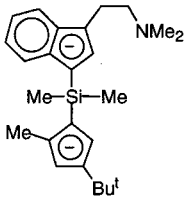
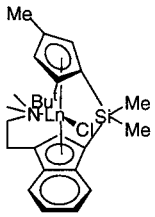
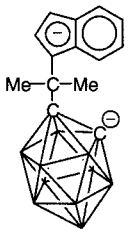
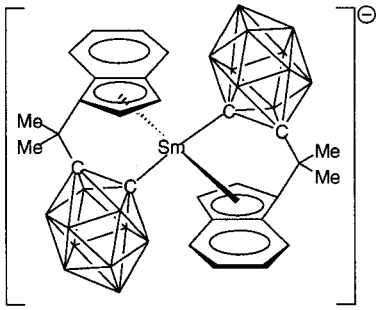
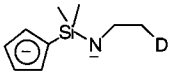
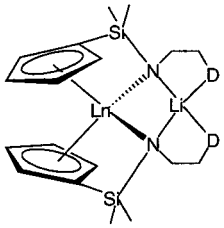
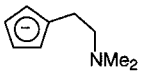
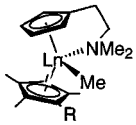
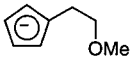
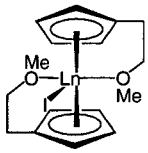
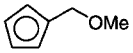
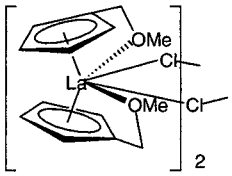
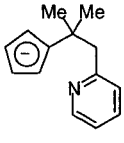
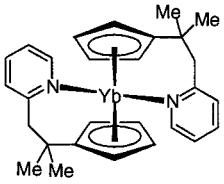
Entry	Ligand	Complex	Ref
8		 X=Cl or Me	244
9			245
10			246
11			247
12			248
13			249,250
14			251
15			252

Table 2. Chiral Lanthanide Bis(cyclopentadienyl) Complexes Isolated Enantiomerically Pure

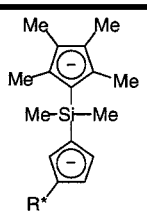
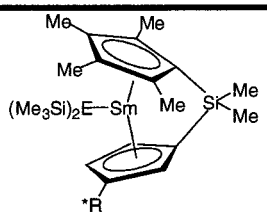
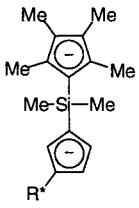
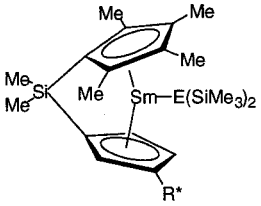
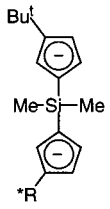
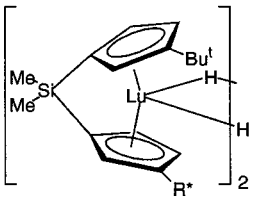
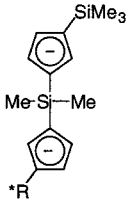
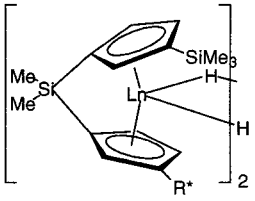
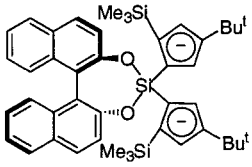
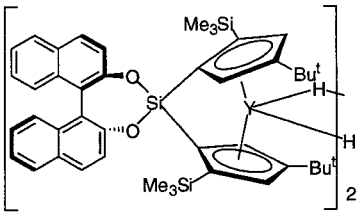
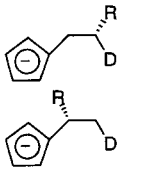
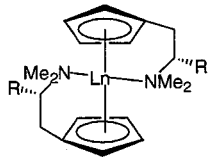
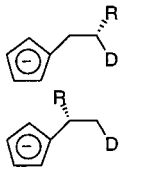
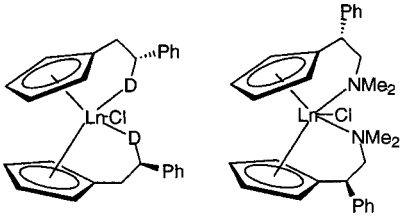
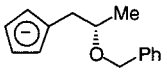
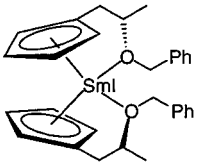
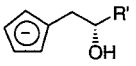
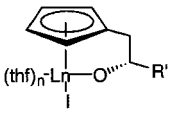
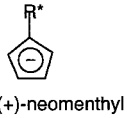
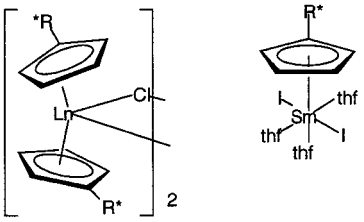
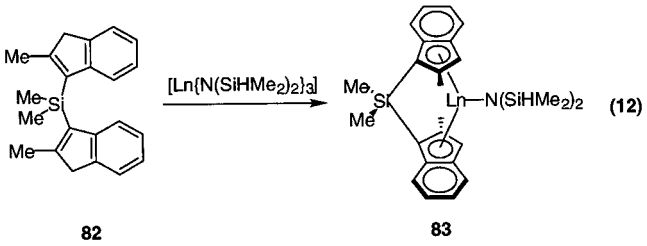
Entry	Ligand	Complex	Ref
1	 R*=menthyl	 E=N or CH	145
2	 R*=neo-menthyl	 E=N or CH	145
3	 R*=(+)-neomenthyl		222
4	 R*=menthyl		223
5			143
6	 R=Me or Ph D=OMe or NMe_2	 Ln=Sm or Yb	147
7	 R=Me or Ph D=OMe or NMe_2		148

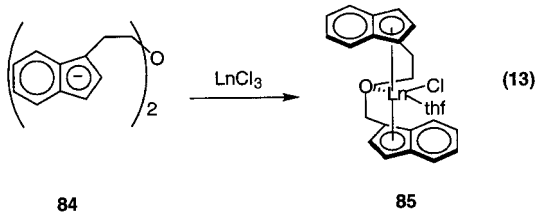
Table 2. Chiral Lanthanide Bis(cyclopentadienyl) Complexes Isolated Enantiomerically Pure

Entry	Ligand	Complex	Ref
8			253
9			254
10	 R*=(+)-neomenthyl		255



82 83

(12)



84 85

(13)

formed in a ratio of 6:1 *rac*:*meso* as shown in reaction 13.[141,142] The crystal structure of complex **85** (Ln = Nd) is shown in Figure 33. Silylamide derivativesmay be prepared by the metathesis of chloro complexes **85** with $LiN(SiMe_3)_2$.

None of the complexes described so far has been isolated in enantiomerically pure form. To achieve this without resorting to sophisticated resolution techniques, an enantiomerically pure chiral component must be incorporated into the ligand. This can be achieved either by using a chiral linker or by incorporating a chiral substituent into a ring. There are two examples of the use of a chiral bridging group in a linked cyclopentadienyl ligand system. Bercaw used a binaphtholate-substituted Si as a linker in ligand **86**.

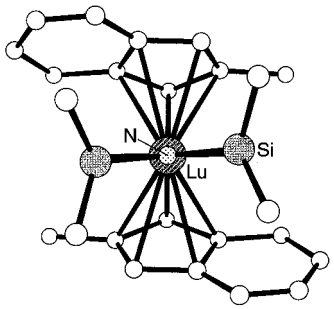


Figure 32. Structure of complex **83**.

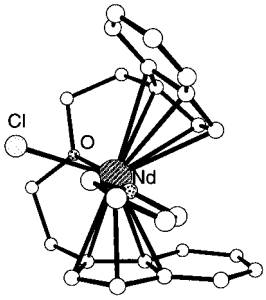
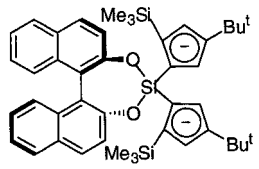
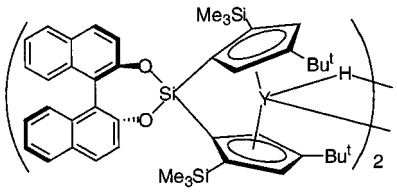


Figure 33. Structure of complex **85** (Ln = Nd).



86



87

Steric interactions between the 3 and 3′ H's of the binaphtholate group and the Me_3Si substituents on the cyclopentadienyl rings force the ligand to bind in a diastereoselective manner to give the C_2-symmetric complex [YCl(**86**)(thf)], with the *R*-binaphtholate-**86** giving selectively *S*-[YCl(**86**)(thf)]. The alkyl species [Y(**86**)$(CH(SiMe_3)_2]$ can be generated by reac-

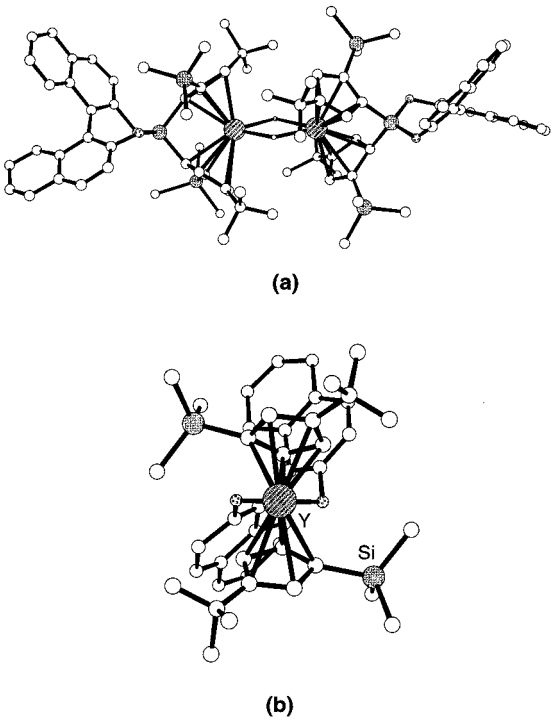
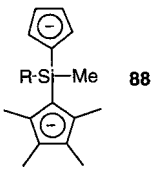


Figure 34. Structure of complex **87**: (a) view of whole molecule and (b) view of one-half of dimer (H atoms omitted for clarity).

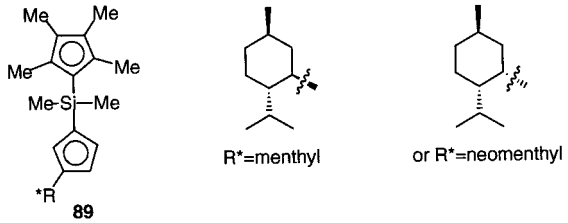
tion with $LiCH(SiMe_3)_2$, and subsequent reaction with H_2 results in formation of the hydride-bridged dimer **87**, which has been characterized crystallographically.[143] Some views of the crystal structure are shown in Figure 34.

Schumann employed an unsymmetrically substituted Si as a linker in the bridged Cp ligand **88**. However, this ligand and its complexes have not yet been isolated enantiomerically pure.[144]



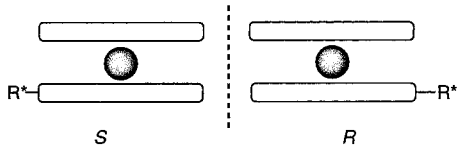
88

Marks addressed the problem of preparing a readily isolable enantiomerically pure bis(cyclopentadienyl) by incorporating a single chiral substituent into a linked Cp ligand **89**.[145]



89

The possible structures of the product can be represented schematically as shown below.



Because the substituent on the Cp ring is itself chiral, the two structures represented as *S* and *R* are diastereomers rather than enantiomers and are therefore potentially separable without resorting to sophisticated chiral resolution techniques. This ligand system was found to give high diastereoselectivity (>80%) in complexation with the lanthanides, and it is possible to obtain essentially pure single diastereomers of the chloro complexes [Ln(**89**)(μ-Cl)$_2$Li(thf)$_2$] by a single recrystallization from Et_2O. However, epimerization via Cp ring detachment and rotation about the Si−Cp bond occurs slowly in donor solvents, with the equilibrium diastereomer ratio depending on the solvent.

Preparation of organo or amido derivatives from the LiCl adducts results in further epimerization when R* = neomenthyl. However, the amidation or alkylation of *R*-menthyl complexes proceeds with retention of configuration. These preparative reactions are summarized in Scheme 4. The structures of *R*-**93** (Ln = Sm; E = CH) and *S*-**92** (Ln = Sm; E = CH) are shown in Figures 35 and 36.

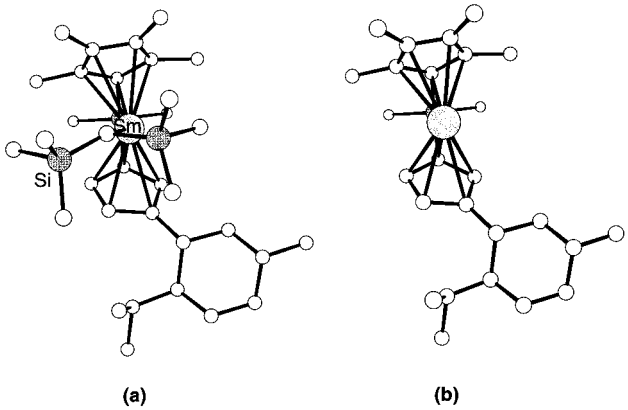


Figure 35. (a) Structure of *R*-**93** (Ln = Sm; E = CH) with (b) $CH(SiMe_3)_2$ omitted for clarity.

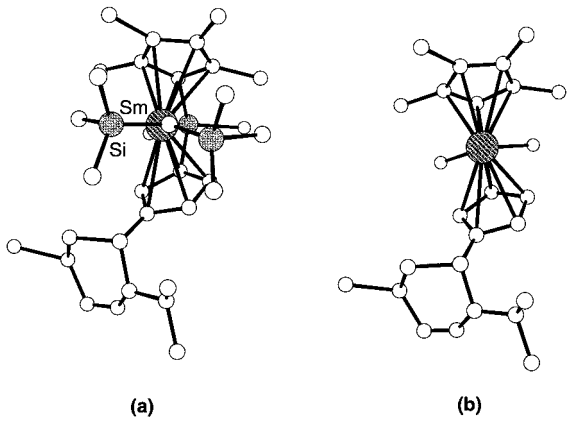
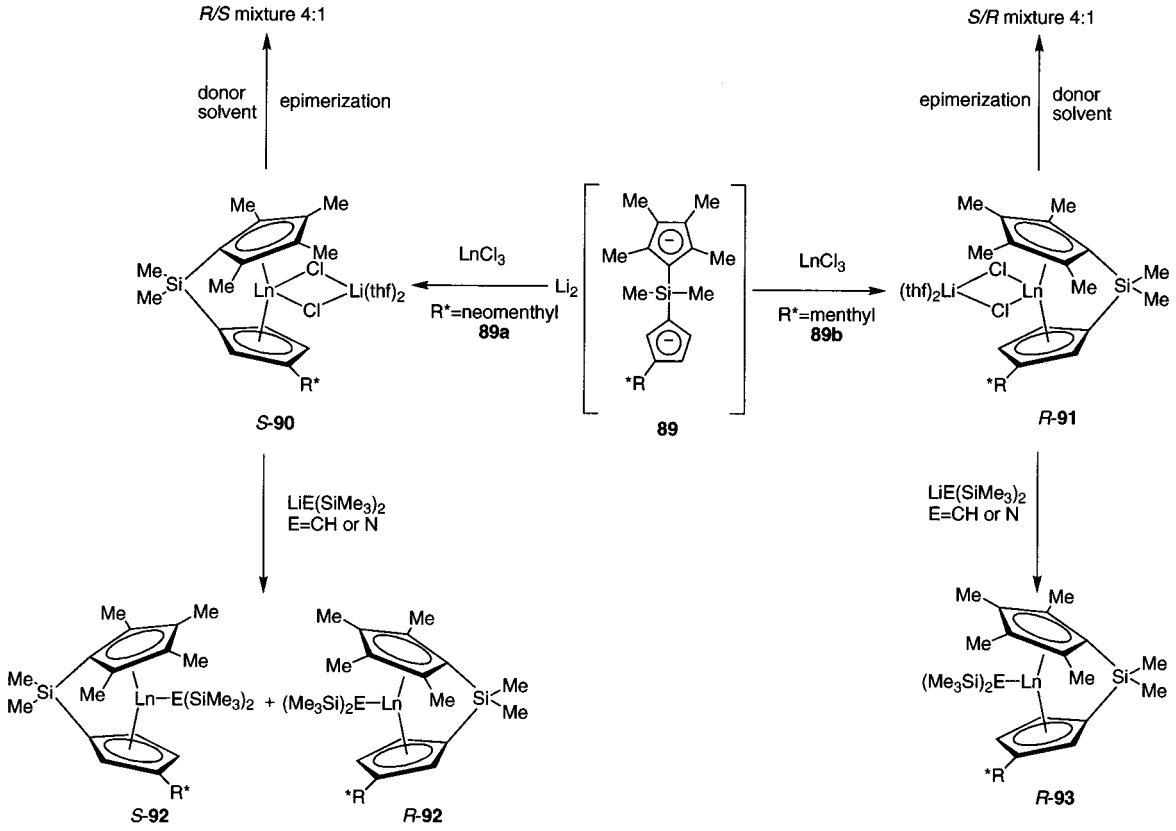


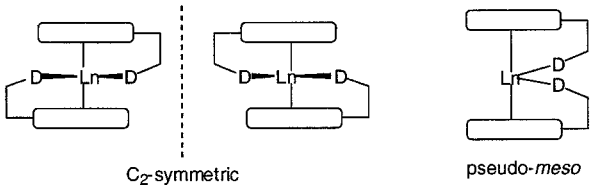
Figure 36. (a) Structure of *S*-**92** (Ln = Sm; E = CH) with (b) $CH(SiMe_3)_2$ omitted for clarity.

Scheme 4

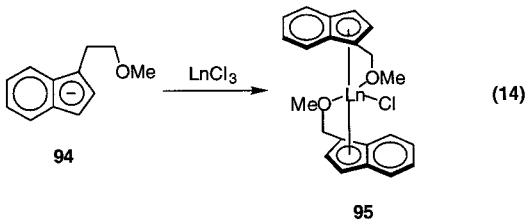


C. Donor-Functionalized Cyclopentadienyl or Indenyl Ligands

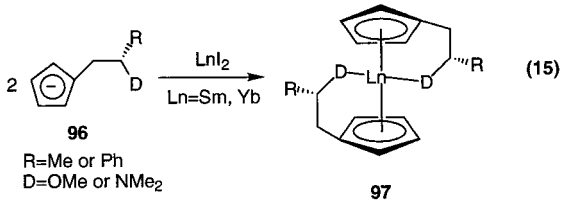
Donor-functionalized Cp ligands can in principle give C_2-symmetric or pseudo-*meso* complexes as represented by the structures below.



Achiral donor-functionalized indenyl ligands **94** have been investigated by Qian, and a *rac*:*meso* ratio of up up to 25:1 is observed for early and late lanthanides as shown in reaction 14.[146]



Preferential formation of the *rac* diastereomer has been achieved in many cases, and incorporation of a chiral donor group as in ligand **96** can result in selective formation of an enantiomerically pure complex. Enantiomerically pure complexes **97** of Sm(II) and Yb(II) have been prepared according to reaction 15.[147]



The crystal structure of complex **97** is shown in Figure 37. Ln(III) chloro complexes with ligand **96** have also been prepared in enantiomerically pure form for Ln = Sm, Y, Lu.[148]

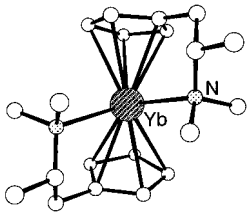
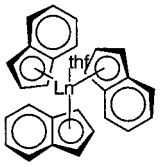


Figure 37. Structure of complex **97** (R = Me; D = NMe_2; Ln = Yb).

D. Unsubstituted Tris(indenyl) Complexes

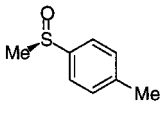
Tris(indenyl) lanthanide complexes $[Ln(C_9H_7)_3(thf)]$ **98** (Ln = Nd, Gd, Er) spontaneously resolve on crystallization in the chiral space group *P*6, with the disordered thf ligand bound along the C_3 axis.[149,150]

Substitution of the thf with C_{3v}-symmetric Ph_3PO results in both enantiomers crystallizing together in

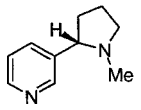


98

a centrosymmetric space group. However, if the chiral sulfoxide ligand **99** is added, the conformation of the indenyl rings is locked to give crystals containing a single enantiomer of [Ln(C_9H_7)$_3$(**99**)].[151] These adducts with chiral sulfoxide have been investigated in solution by CD and NMR spectroscopy.[152] The more remote chiral center of nicotine **100** is not capable of locking the conformation of the indenyl rings.



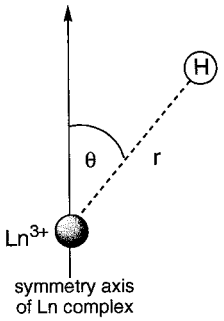
99



100

VIII. Chiral Lanthanide Complexes as NMR Shift Reagents

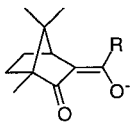
Lewis acidic complexes of paramagnetic Ln^{3+} ions (particularly Pr^{3+}($4f^2$), Eu^{3+} ($4f^6$), and Yb^{3+}($4f^{13}$)) with achiral β-diketonate ligands such as fod ($C_3F_7C(O)$-$CHC(O)Bu^t$) and thd ($Bu^tC(O)CHC(O)Bu^t$) have been well-known as lanthanide shift reagents for many years. They can be used to simplify second-order NMR spectra of Lewis bases such as alcohols, ketones, or amines and were particularly valuable in the days before high-field NMR spectrometers became routinely available. The Lewis basic substrate is present in excess and forms a labile complex with the [Ln(diket)$_3$]. While bound to the paramagnetic Ln^{3+} center, in addition to the external magnetic field, the substrate experiences the local magnetic field due to the unpaired electrons on the Ln ion, and the predominant dipolar interaction between this field and the nuclear spin under investigation leads to a shifting in the NMR spectrum. This dipolar or 'pseudocontact' shift is dependent on geometrical factors including the distance from the Ln^{3+} ion. For axially symmetrical complexes the magnitude of the pseudocontact shift is given by $\Delta\delta = k(1 - 3\cos^2\theta)/r^3$, where r and θ are defined in **101**. Labile shift reagent adducts have time-averaged axial symmetry, and so this equation is applicable.



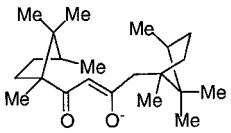
101

The use of an enantiomerically pure Ln Lewis acid as a shift reagent makes it possible to analyze enantiomerically impure chiral substrates. The adducts formed between an enantiomerically pure shift reagent and the enantiomerically impure substrate are diastereomers and therefore have different NMR spectra. The separation of NMR signals, particularly for nuclei close to the Ln ion, is usually good, because of the great sensitivity of the chemical shifts of paramagnetic Ln complexes to geometrical factors. Different association constants between the shift reagent and the enantiomers of the substrate may also contribute to differential shifting of NMR resonances.

The first application of chiral lanthanide complexes was in the NMR analysis of mixtures of enantiomers, and this continues to be an important method.[153,154] Whitesides used a camphor-derived diketonate **1** to prepare the chiral shift reagent [Eu(pvc)$_3$].[5] Since then other camphor-derived lanthanide shift reagents have been introduced, e.g., [Ln(tfc)$_3$],[7] [Ln(hfc)$_3$],[8] and [Ln(dcm)$_3$] (dcm = **2**).[9]

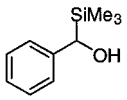


1
tfc R=CF_3
hfc R=C_2F_7
pvc R=Bu^t



2
dcm

These shift reagents work well in noncoordinating solvents such as $CDCl_3$ or C_6D_6; polar substrates such as diols can be analyzed in CD_3CN solvent using [Eu(hfc)$_3$] or [Eu(tfc)$_3$].[155] Although ^{1}H NMR spectroscopy is most commonly used in the determination of enantiomeric purity, the use of ^{29}Si NMR spectroscopy to investigate α-silylated amines and alcohols has also been reported. In the presence of [Eu(tfc)$_3$], a racemic mixture of α-trimethylsilylbenzyl alcohol **102** shows two separate resonances in the ^{29}Si NMR spectrum. This method also works well for α-trimethylsilylamines and aliphatic alcohols.[156]



102

In addition to its wide application in studying chiral organic substrates, [Eu(tfc)$_3$] can also be of use to the coordination chemist: good resolution of the ^{1}H NMR signals of racemic [Ru(phen)$_3$]Cl_2 has been achieved in the presence of [Eu(tfc)$_3$] in CD_2Cl_2 as solvent.[157] An ion-pairing interaction of the type [Ru(phen)$_3$]$^{2+}$−Cl^-−[Eu(tfc)$_3$], with Cl^- lying on the C_3 axis of the metal complexes, was proposed. Resolution of signals was not achieved for the ClO_4^- salt in CD_2Cl_2 or for either salt in d_6-dmso, presumably due to coordination of solvent to the shift reagent. This was the first reported example of the application of chiral lanthanide shift reagents to a cationic species.

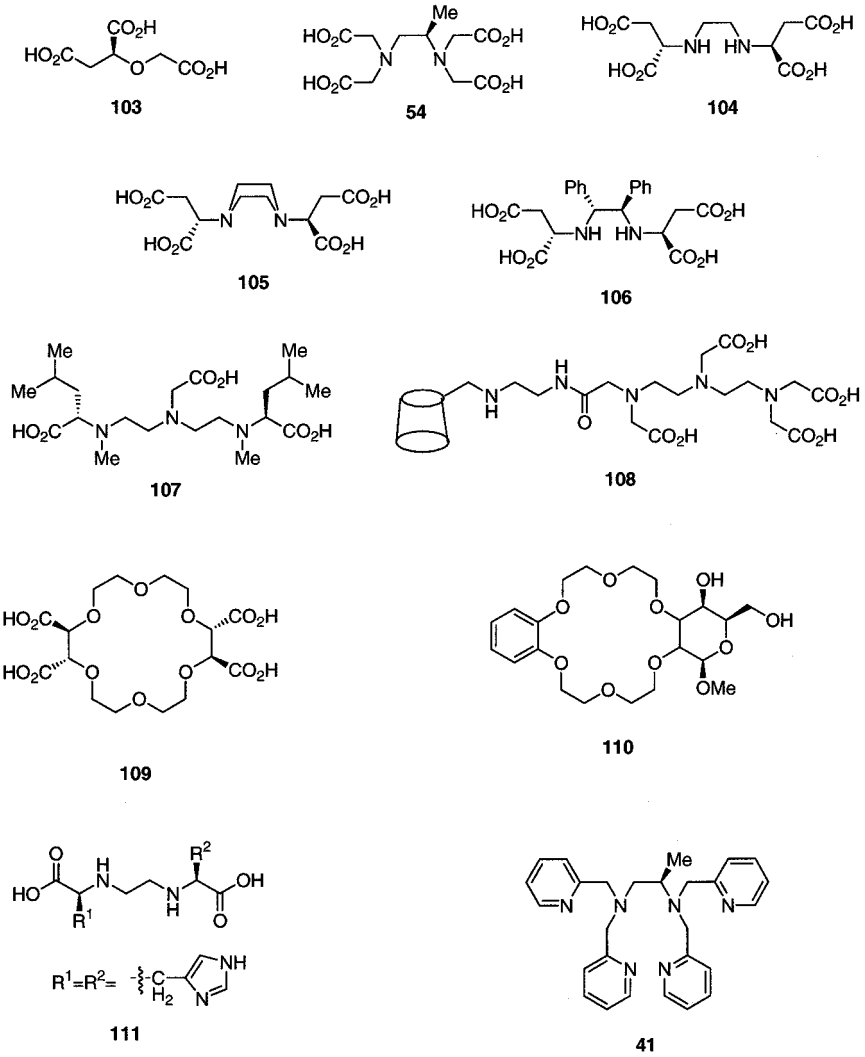


Figure 38. Chiral ligands that have been used in chiral lanthanide shift reagents for use in aqueous solution.

Lanthanide ions are classical 'hard' Lewis acids and so generally show little propensity to bind to donors other than 'hard' O or N Lewis bases. NMR study of 'soft' chiral substrates such as alkenes therefore requires some modification to the simple chiral lanthanide shift reagent. Wenzel[158,159] reported the use of a binuclear Ln(III)−Ag(I) shift reagent prepared as shown in reaction 16.

$$[Ln(hfc)_3] + [Ag(hfc)] \rightarrow Ag[Ln(hfc)_4] \quad (16)$$

The structure of this chiral shift reagent has not been established crystallographically, but it is proposed to be a binuclear complex (this was confirmed by mass spectrometry) in which the soft Ag atom binds to soft donors such as C=C double bonds and the neighboring Ln ion causes the paramagnetic shifting. This system has been applied successfully to the study of terpenes.

The $[Ln(hfc)_3]$ and $[Ln(tfc)_3]$ complexes discussed above work well with a range of substrates, but their use is limited to nonaqueous solutions, and so of course they cannot be applied to α-amino acids. Determination of the enantiomeric purity of this important class of chiral molecules requires a different type of chiral shift reagent. Because of the large enthalpies of hydration of Ln^{3+} ions and the lability of their complexes, the synthesis of chiral Ln complexes that are stable in aqueous solution is a significant challenge. The structures of some ligands used for synthesis of chiral lanthanide shift reagents for use in aqueous solution are summarized in Figure 38. Most of these ligands are carboxylates, and many of them are derived from well-known polyaminocarboxylates such as DTPA (diethylenetriaminepenaacetic acid).

The first chiral lanthanide shift reagent reported to resolve α-amino acids was prepared by reaction of $Ln_2(CO_3)_3$ with *S*-carboxymethyloxysuccinic acid (**103**).[160] This reagent is effective in aqueous solution at pH 3; however, self-association of the complex has been reported to cause some problems. Kabuto then reported the Eu complex of *R*-propylenediaminetetraacetate **54** as a valuable shift reagent for use in aqueous solution. This complex is stable over a pH range of 1.5−13.0 and has a stability constant comparable to that of the corresponding EDTA complex. Resolution of NMR resonances from α-hydroxy and α-amino acids was achieved at pH ∼ 9.[161] Subsequent work has demonstrated that, in contrast to $[Ln(hfc)_3]$ and $[Ln(tfc)_3]$ chiral shift reagents, there is a highly consistent correlation between the absolute configuration of the substrate and the induced

shift. This has been demonstrated for α-amino acids,[162] α-hydroxy carboxylic acids,[163] α-Me-α-amino acids,[164] and aldonic acids.[165] Separation of the enantiomer resonances by complexes of **54** is due to different association constants between the chiral shift reagent and the enantiomers of the substrate.

A problem often associated with the use of chiral lanthanide shift reagents is severe line broadening when using high-field spectrometers. This is due to exchange between free and coordinated substrate and therefore poses a greater problem with larger induced shifts. This problem has been overcome by the use of a Sm complex of **54**.[166] The Sm complex gives rise to much smaller induced shifts than the Eu complex and hence may be used at much higher fields without significant line broadening. It is effective with a large range of substrates.

The Eu complex of *S,S*-ethylenediamine-*N,N′*-disuccinate **(104)** also allows enantiomeric separation of some amino acids. This complex has log $K = 13.54$ and is an effective chiral shift reagents for some α-amino acids in the pH range 9−11.[167] Other succinate derivatives **105** and **106** are also found to be effective in this pH range.[168]

Resolution of α-amino acid signals using the shift reagents discussed so far requires pHs in the range 9−11. A small number of complexes are available that function best at close to neutral pH. For example, complexes with the diethyleenetriamine-derived ligand **107** are effective for amino acids and N-protected oligopeptides at pH 7−8.[169] A Eu complex of the polypyridyl ligand **41** is also effective at neutral pH, and as with the propylenediaminetetraacetate complexes, consistent shifting is observed for the α-protons of α-amino acids.[59] Unprotected amino acids have also been analyzed at neutral pH by Eu^{3+} complexes of *N,N′*-ethylenebis(amino acid) ligands such as **111**.[170]

The commercially available 18-crown-6 derivative **109** can be used in aqueous solution with approximately 5 mol equiv of $Yb(NO_3)_3$. This system gives good separation (0.1−0.2 ppm) for D,L-alanine methyl ester hydrochloride.[171] The galacto pyranoside-derived crown ether **110** gives enhanced resolution of alanine esters in the presence of $Yb(NO_3)_3$. Surprisingly the combination of $Dy(NO_3)_3$ and **110** is completely ineffective: Dy^{3+} gives the largest dipolar shifts and its failure in this instance is ascribed to an inability to complex with **110**.[172] The Dy^{3+} complex of the cyclodextrin-functionalized aminocarboxylate ligand **108** can be used in aqueous solution to analyze substrates that form inclusion complexes with cyclodextrins. In this case the enantiomeric discrimination is due to substrate association with the cyclodextrin rather than with the Dy^{3+}, which just serves to enhance the signal separation.[173]

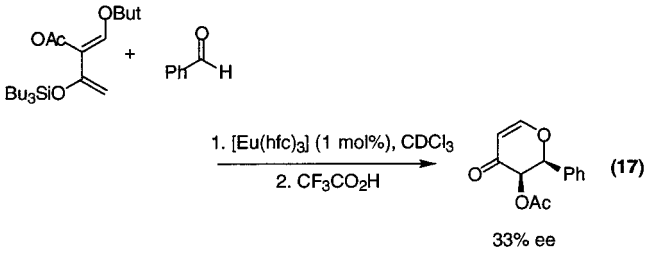
Quantitative analysis of mixtures that have high enantiomeric purity (>95%) may be difficult due to the difficulty of identifying NMR resonances due to the minor enantiomer. This problem may be overcome by the use of a calibration plot: a plot of the induced shift in one enantiomer vs the induced shift in the other enantiomer at various shift reagent concentrations gives a straight line. The position of the resonance of the major enantiomer can therefore be used to predict the position of the resonance of the minor enantiomer. Once the position of the resonance was established, integration measured enantiomeric purities as high as 99.7% ee.[174]

IX. Enantioselective Catalysis by Chiral Lanthanide Complexes

This discussion of enantioselective catalysis by Ln complexes is organized according to chiral ligand type in order to emphasize the effectiveness of different classes of ligand in defining effective chiral binding sites. The discussion will begin with complexes containing anionic chiral ligands (diketonates and alkoxides, including binaphtholates), followed by neutral chiral ligands (including binaphthol and bis(oxazoline)s, and will finish with chiral organolanthanide complexes.

A. Diketonate Complexes

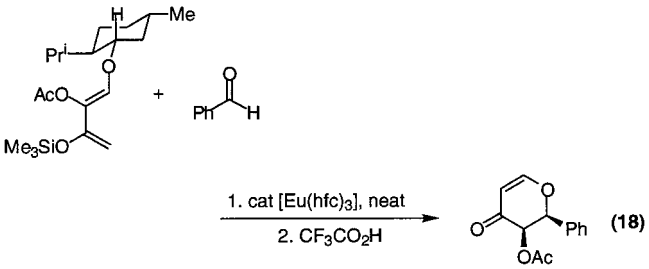
The first example of enantioselective Lewis acid catalysis by a chiral lanthanide complex was reported by Danishefsky in 1983.[175] The hetero-Diels−Alder reaction had previously been shown to be catalyzed by achiral lanthanide tris(β-diketonates) such as Eu(fod)$_3$ (fod = $Bu^tC(O)CHC(O)C_3F_7$), and use of the chiral analogue [Eu(hfc)$_3$] resulted in a modest ee of 33% in reaction 17.



(17)

33% ee

Subsequent optimization of reaction conditions (−10 °C, no solvent) improved the ee to 58%; increasing the catalyst loading did not increase the ee, although the rate of reaction was increased.[176] When a chiral (L-menthyl) auxiliary was attached to the diene, the reaction was catalyzed by [Eu(hfc)$_3$] to give product in 86% ee as shown in reaction 18. The achiral [Eu(fod)$_3$] complex resulted in only 10% ee in this reaction, demonstrating the importance of the interaction between the chiral substrate and the chiral catalyst.

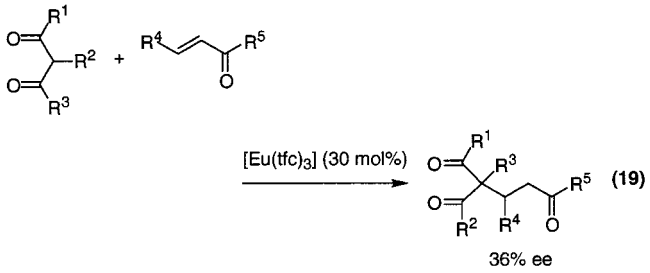


(18)

86% ee

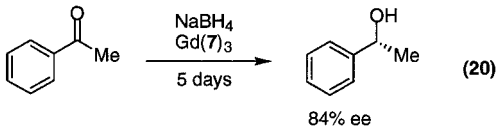
The chiral lanthanide shift reagent [Eu(tfc)$_3$] (see sections II.A.1 and VIII) has been used to catalyze

the enantioselective Michael addition of 1,3-dicarbonyl compounds as shown in reaction 19.[177] The catalyst loading here is high, and the ee obtained is only modest.



(19)

A L-menthyloxy-substituted β-diketonate ligand **7** has been used to prepare a chiral lanthanide tris(β-diketonate) where noncovalent interactions between ligands lock the conformation of the complex (see section II.A.1),[11] and the Gd complex has been used to catalyze the enantioselective borohydride reduction of ketones as shown in reaction 20. Although a stoichiometric quantity of the Gd complex is required, it can be recovered intact at the end of the reaction.



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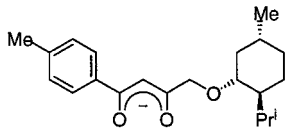
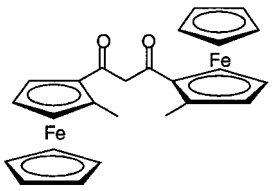


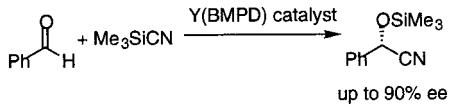
7

The bis(ferrocenyl) diketone 1,3-bis(2-methylferrocenyl)propane-1,3-dione (HBMPD; **112**) reacts with $Y(OPr^i)_3$ (probably best formulated as $[Y_5O(OPr^i)_{13}]$) to give a diketonate complex that is an active catalyst for the enantioselective silylcyanation of aldehydes.[178]



HBMPD
112

Although the exact nature of the active catalyst has not been determined, it has been shown that [Y(BMPD)$_3$] gives poor enantioselectivity in the reaction. The catalyst formed from 1 equiv of BMPD per Y gives the best results as shown in reaction 21.[179]



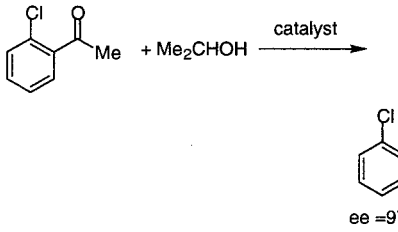
(21)

B. Alkoxide Complexes

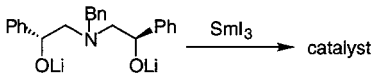
Lanthanide alkoxides can act as both Lewis acids (due to the coordinative unsaturation at the Ln atom) and Brønsted bases due to the primarily ionic nature of the Ln−alkoxide bond. They show catalytic activity in many achiral reactions, and there are now several examples of enantioselective catalysis by chiral lanthanide alkoxides. In most cases the catalyst is generated in situ and has not been characterized. Shibasaki's heterometallic alkali-metal lanthanide binaphtholates are the most successful and most thoroughly characterized enantioselective lanthanide alkoxide catalysts to date, and their chemistry is so extensive that it will be dealt with separately in section IX.C.

1. Meerwein–Ponndorf–Verley Reductions

The Meerwein−Ponndorf−Verley reduction of ketones by an alcohol is catalyzed very effectively by small quantities of lanthanide alkoxides. A highly enantioselective version of this reaction (reaction 22**)** has been reported by Evans.[180] The catalyst is prepared in situ by reaction of a dilithium aminoalkoxide with SmI_3 (reaction 23) but has not been isolated or characterized further.

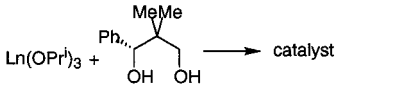


(22)

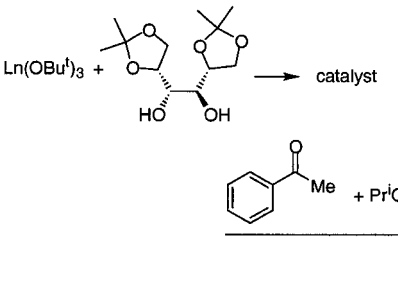


(23)

Less impressive results have been obtained from catalysts prepared in situ by addition of chiral diols to $Ln(OPr^i)_3$[181] or $Ln(OBu^t)_3$[182] as shown in reactions 24 and 25.



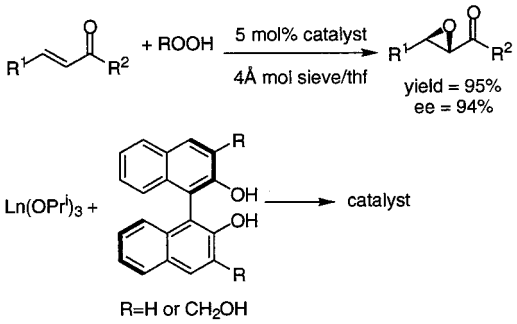
(24)



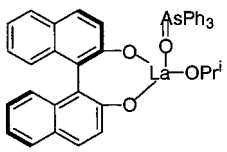
(25)

2. Epoxidation of Enones

Catalysts prepared by reaction of $Ln(OPr^i)_3$ with 1 equiv of binaphthol have been used in enantioselective oxidation of enones (reaction 26).[183−185]



The catalyst (not yet structurally characterized) was found to be effective for epoxidation a wide range of substrates, unlike the heterometallic M_3[Ln(binol)$_3$] catalysts (section IX.C). The effect on enantioselectivity of substituents in the 3 and 6 positions of binaphthol has been investigated. Bulky substituents (e.g., $SiMe_3$ or Br) in the 3 and 3′ positions result in poor enantioselectivity (8% and 14% ee, respectively),[184] whereas methoxymethyl in the 3 position gives excellent results. Enantioselectivity is also sensitive to substitution at the more remote 6 and 6′ positions: 6,6′-dibromo- and 6,6′-diphenylbinaphthol both give enhanced enantioselectivity compared with the unsubstituted binaphthol. Addition of triphenylphosphineoxide[186] or triphenylarsine oxide[22] at the catalyst preparation stage results in enhanced selectivity. This modified catalyst has not been characterized but is proposed to have a monomeric structure **113**.

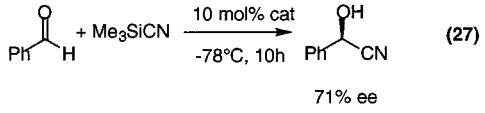


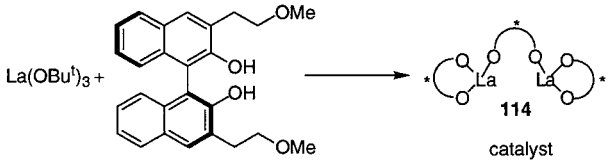
113

Positive nonlinear effects have been observed in this reaction and have been ascribed to formation of a stable [La(*R*-binol)(*S*-binol)] complex which is catalytically inactive.

3. Silylcyanation of Aldehydes

Achiral lanthanide alkoxides catalyze the silylcyanation of aldehydes reaction 27, probably via a lanthanide cyanide as the active catalyst. Enantioselective catalysts for this reaction have been prepared in situ by reaction of La(OBu^t)$_3$ with H_2binol and 3,3′-substituted derivatives.[187] The best results were obtained with methoxyethyl substituents. A

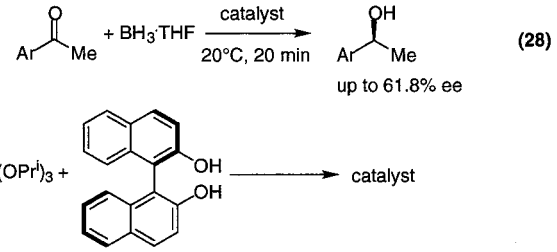




dinuclear structure **114** has been proposed for the catalyst, but it has not been isolated or characterized.

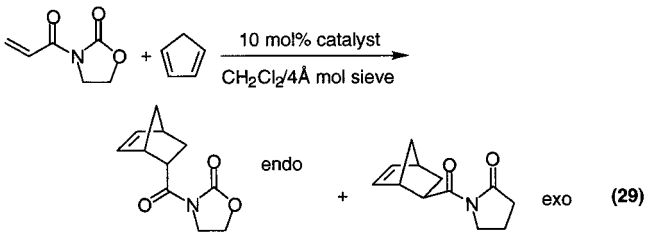
4. Borane Reduction of Ketones

A catalyst prepared in situ by reaction of La(OPr^i)$_3$ with binaphthol has been used to catalyze borane reduction of prochiral ketones with modest enantioselectivity (reaction 28).[188]

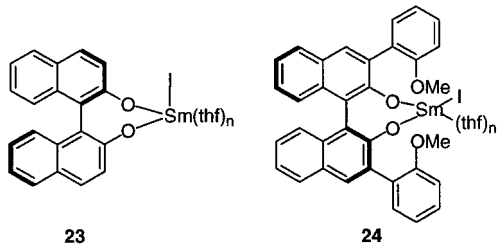


5. Diels–Alder Reactions

Lanthanide iodides have been investigated as a new class of Lewis acid catalysts,[189] and heteroleptic samarium binaphtholate iodide complexes have been used to catalyze the Diels−Alder reaction 29.



When complex **23**, which contains an unsubstituted binaphtholate ligand, is used, the maximum of 28% ee is achieved at −25 °C. Complex **24**, with methoxyphenyl substituents in the 3 and 3′ positions, results in an ee of 81% at −28 °C. On lowering the temperature to −60 °C, a *reversal* of ee is observed; the magnitude of this reversed ee is 30%.[28] Catalysts **23** and **24** have been characterized spectroscopically but not by X-ray diffraction.

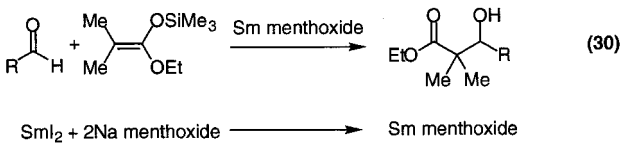


23 **24**

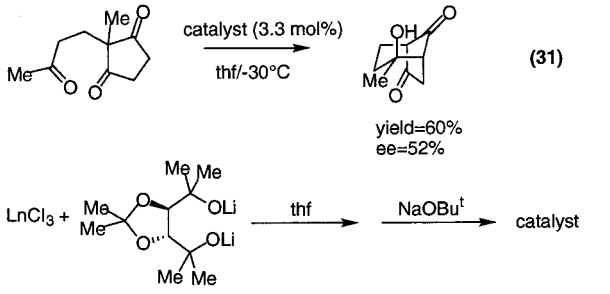
6. Aldol Reactions

A Sm(II) menthoxide has been reported to promote the Mukaiyama aldol reaction 30, but only modest ee's were achieved. The best enantioselectivity (30%) is obtained using 2 equiv of Sm menthoxide, but the yield is only 16%. An improved yield of 92% is obtained using 0.2 equiv of Sm menthoxide, but in this case the ee is reduced to 2%.[190]

A chiral lanthanide alkoxide incorporating a TADDOLate ligand **115** catalyzes an intramolecular aldol reaction with 52% ee as shown in reaction 31. This



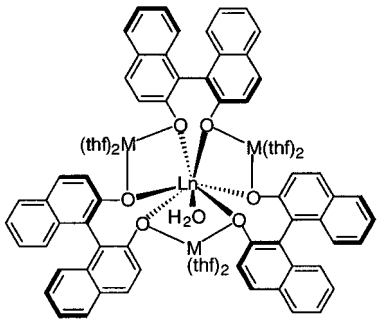
lanthanide complex, which has not been characterized, also catalyzes the nitroaldol reaction but with no asymmetric induction.[17] The catalyst prepared using binaphthol as the chiral diol gives an excellent ee of up to 90% in the nitroaldol reaction, and this was the starting point for development of the Shibasaki heterometallic alkali-metal lanthanide binaphtholates, which are the subject of the next section.



Li_2**115**

C. Heterometallic $M_3[Ln(binol)_3(H_2O)]$ Complexes

Heterometallic $M_3[Ln(binol)_3]$ catalysts **20** were first used by Shibasaki[17] and characterized the following year.[19] The structures of these complexes have already been discussed in section II.A.3, and their applications to a range of enantioselective reactions have been reviewed[191,192] and form the subject of another article in this issue. Only a brief summary of the main features of the catalysts and their reactions will be given here.



20

The unique feature of $M_3[Ln(binol)_3]$ is that they can act as bifunctional catalysts: the Ln is Lewis acidic and the binol ligands can act as a Brønsted base. This bifunctional behavior has been compared with that of enzymes. The catalysts have been applied to the following reaction types, which are summarized in Table 3: (1) Asymmetric C−C bond formation, Nitroaldol reaction (entry 1), aldol reaction (entry 2), Michael addition reaction (entry 3), and Diels−Alder reaction (entries 4a and 4b); (2) Asymmetric C−O bond formation, epoxidation of enones (entry 5); (3) Asymmetric C−P bond formation,

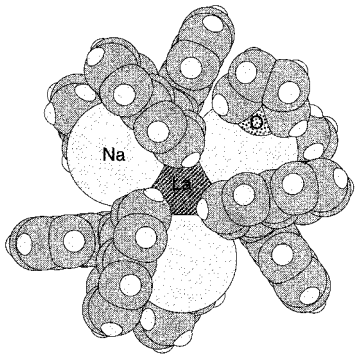


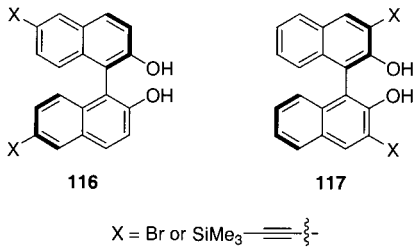
Figure 39. Space-filling picture of $[Na(thf)_2][La(S\text{-binol})_3(H_2O)]$ viewed along the 3-fold axis.

hydrophosphonylation of aldehydes (entry 6) and of imines (entry 7).

Enantioselective hydrophosphonylation reactions of aldehydes have also been catalyzed by catalysts generated in situ by the reaction of Li_2binol with $LaCl_3$[193] or by the reaction of a 3,3′-bis(methoxyethyl) binaphthol with NaOBu^t an $LaCl_3$.[194] Although not stated explicitly in the original publications, the active catalysts in these reactions are almost certainly of the $M_3[Ln(binol)_3]$ type.

A space-filling picture of $[Na(thf)_2][La(S\text{-binol})_3(H_2O)]$ is shown in Figure 39, illustrating the well-defined chiral binding site that results in high enantioselectivities. There are three relatively straightforward ways in which these catalysts may be fine-tuned to give optimum performance for a particular reaction: variation of M, variation of Ln, and introduction of substituents into the binol ligands. All of these options have been explored to some extent.

Introduction of substituents (Br or trimethylsilylethynyl) into the 6 and 6′ positions of the binol as in **116** has resulted in improved enantioselectivities in both the nitroaldol and Diels−Alder reactions, whereas substituents in the 3 and 3′ positions as in **117**, which are closer to the Ln atom, have a detrimental effect on enantioselectivity.

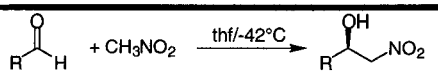
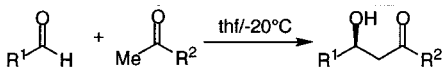
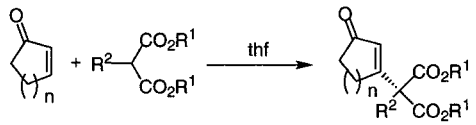
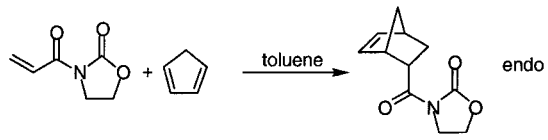
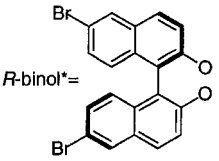
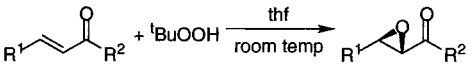
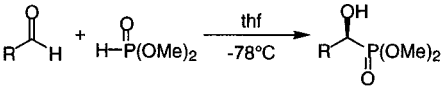
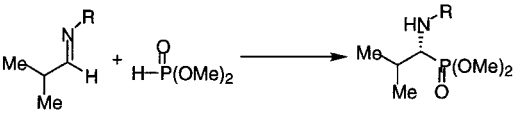


116 **117**

X = Br or $SiMe_3$—≡—

The choice of alkali metal is crucial, e.g., Li gives the best results for hydrophoshonylation of aldehydes (Table 3, entry 6) whereas K gives the best results for hydrophosphonylation of imines (Table 3, entry 7). In the enantioselective epoxidation of enones, the presence of alkali metal can be detrimental. Although the example given in Table 3 entry 5 works well with $Na_3[La(R\text{-binol})_3(H_2O)]$, this catalyst is not applicable to a wide range of substrates. A more generally applicable catalyst for the epoxidation reaction is an alkali-metal-free complex prepared in situ by reaction of $[La(OPr^i)_3]$ with a 3-hydroxymethyl *R*-binaphthol as described in section IX.B.

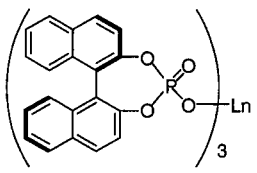
Table 3. Enantioselective Reactions Catalyzed by $M_3[Ln(binol)_3(H_2O)]$ Complexes

Entry	Reaction	Catalyst	%ee	Ref
1		$Li_3[La(S\text{-binol})_3(H_2O)]$	90 (R=cyclohexyl)	17
2		$Li_3[La(R\text{-binol})_3(H_2O)]$	≤94	256
3		$Na_3[La(R\text{-binol})_3(H_2O)]$	≤92	257 20
4a	 endo	$Li_3[La(R\text{-binol})_3(H_2O)]$	63	258
4b		$Li_3[La(R\text{-binol*})_3(H_2O)]$	86	258
				
5		$Na_3[La(R\text{-binol})_3(H_2O)]$	83	183
6		$Li_3[La(R\text{-binol})_3(H_2O)]$	95	259
7		$K_3[La(R\text{-binol})_3(H_2O)]$	96	260

Structural studies of anhydrous analogues of Shibasaki's catalysts have shown that there are some quite profound differences in coordination chemistry as M and Ln are varied.[25]

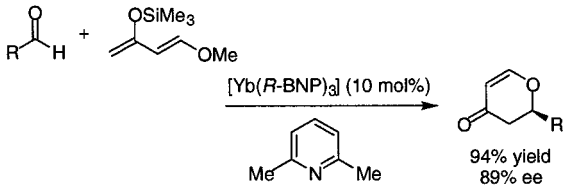
D. Phosphate Complexes

Lanthanide salts **118** of the chiral phosphate BNP have been prepared by reaction of NaBNP with $LnCl_3$ in aqueous solution (see section II.A.5).[34]



118

These chiral salts have been used for enantioselective catalysis of the hetero-Diels−Alder reaction 32, and the addition of amines can result in improved enantioselectivity. 2,6-Lutidine gives the best results (89% ee) compared with 70% ee with no additive; bipy results in very low yields and only 17% ee.[195]



(32)

Impressive asymmetric amplification has been observed with this system: catalyst of 20% ee results in product with 80% ee. This result is obtained both with a mixture of *RRR*- and *SSS*-$[Yb(BNP)_3]$ or with the salt prepared from a mixture of *R*-NaBNP and *S*-NaBNP. The observation has been explained by the formation of *RRS*-/*SSR*-$[Yb(BNP)_3]$ and *RRR*-/*SSS*-$[Yb(BNP)_3]$ pairs which are insoluble and precipitate

out of solution, thus being rendered catalytically inactive.[196]

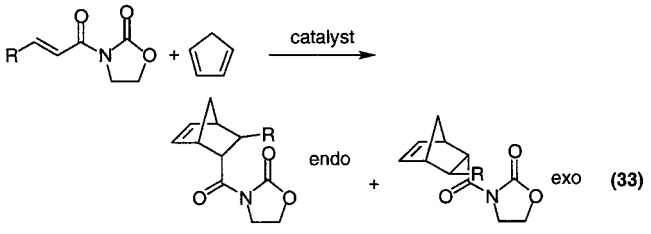
E. Neutral O- or N-Donor Complexes

The application of lanthanide triflates $Ln(OTf)_3$ as mild, selective, and reusable Lewis acid catalysts in organic synthesis is well established,[197−199] and they have been shown to catalyze many important C−C bond-forming reactions including carbonyl allylation, aldol, Michael, and Diels−Alder reactions. $LnCl_3$ compounds are less convenient to handle than $Ln(OTf)_3$, but nevertheless they show useful catalytic properties, e.g., in the silylcyanation of aldehydes. Enantioselective versions of all of these catalytic reactions would be of great value, and progress toward this goal began in 1993 with Kobayashi's initial work on binaphthol-modified $Ln(OTf)_3$ catalysts.[200] Since then, several chirally modified $Ln(OTf)_3$ catalysts have been developed using a range of neutral chiral ligands. Table 4 summarizes these catalytic systems in order to highlight the effectiveness (or otherwise) of the chiral ligands.

Decrease in Ln^{3+} radius generally results in increased catalytic activity and often in increased enantioselectivity. Lu^{3+} is the smallest Ln^{3+}, but due to its high price, Yb^{3+} is normally used instead; Sc^{3+} is sometimes chosen for its enhanced activity (although its cost is significantly higher than that of Yb), and although not a lanthanide, some examples of $Sc(OTf)_3$ catalysis will be considered here. The application of $Ln(OTf)_3$ catalysts in organic synthesis forms the subject of another article in this issue, so only a brief overview will be given here, focusing on the ligand types that are successful in enantioselective catalysis.

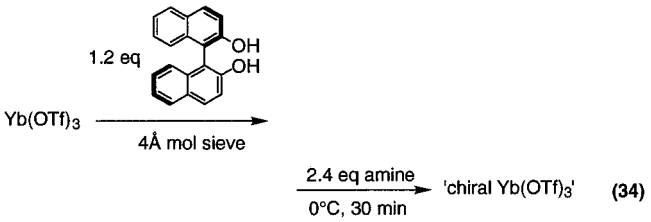
1. Ln(OTf)$_3$ Catalysts Containing Neutral Binaphthol

The Diels−Alder reaction 33 was the first reaction to be investigated in the quest for enantioselective $Ln(OTf)_3$ catalysts, and $Yb(OTf)_3$ was chosen because of its excellent activity and good diastereoselectivity in the achiral version of this reaction.



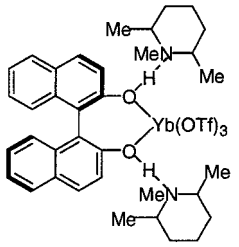
(33)

The chiral $Yb(OTf)_3$ catalyst was prepared in situ according to reaction 34.



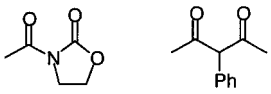
(34)

Optimization of reaction conditions showed that bulky amines were the most effective, and the use of 1,2,6-trimethylpiperidine resulted in an ee of 90% when the reaction was performed at 23 °C, increasing to 95% at 0 °C. ^{13}C NMR and IR spectroscopy have been used to investigate the chiral $Yb(OTf)_3$ catalysts in solution. On the basis of the chemical shift of the NMe group of the base and the IR absorptions in the region 930−1000 cm^{-1}, weak H-bonding between the amine N and the binaphthol OH was identified, and structure **119** has been proposed.[29] In this proposed structure it is the H-bonded amines that define the chiral binding site at Yb and the binaphthol is perhaps best considered as a chiral linker.



119

As a result of investigations into catalyst aging processes, it was discovered that addition of dicarbonyl **120** during the catalyst preparation stage prevented catalyst aging, and the *endo* adduct was obtained in high yield and 93% ee with the absolute configuration 2*S*,3*R* (Table 4, entry 1b). A surprising observation was that addition of diketone **121** resulted in a *reversal* of enantioselectivity and *endo* adduct of 2*R*,3*S* absolute configuration was obtained in 81% ee (Table 4, entry 1c). This was the first observation of a reversal of ee by addition of an achiral additive.[201,202]



120 **121**

The structure of the catalyst is not known, but it seems likely that the dicarbonyl additive increases the coordinative saturation of the $Ln(OTf)_3$ catalyst and thus prevents formation of inactive aggregates. The mechanism by which the identity of the dicarbonyl additive determines the enantioselectivity of the reaction is not known, but this effect appears to be specific to the Diels−Alder reaction.

The $Yb(OTf)_3/H_2$binol/bulky amine catalyst system can be applied to the enantioselective aza Diels−Alder reaction 35 (Table 4, entry 2) provided that the imine can coordinate to Yb in a bidentate manner. Careful choice of amine is also required: when 1,2,6-trimethylpiperidine was used, the ee of product was only 6%. The best results were obtained using a combination of DBU and 2,6-di-*tert*-butyl-4-meth-

Table 4. Enantioselective Catalysis by Chirally Modified $Ln(OTf)_3$

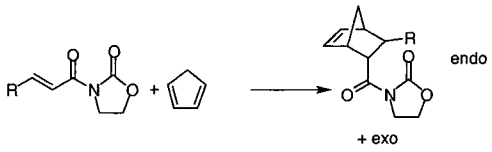
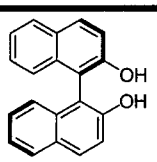
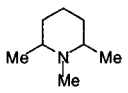
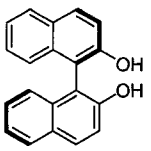
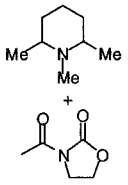
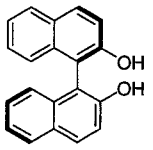
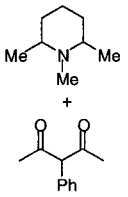
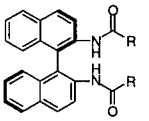
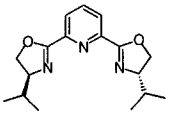
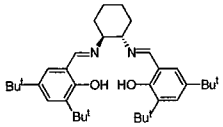
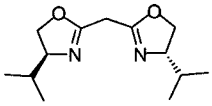
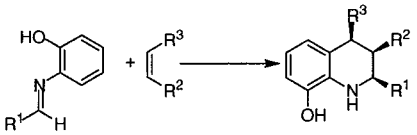
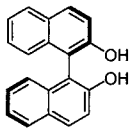
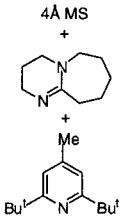
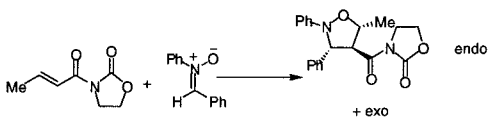
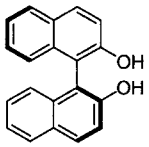
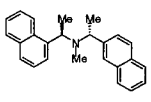
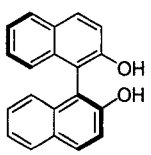
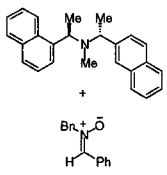
Entry	Reaction	Chiral ligand	Other additive	Max. ee achieved (Ln)/%	Reference
1a			4Å MS + 	90 (Yb)	200,29
1b				93 (Yb)	201
1c				-81 (Yb)	201
1d			Pr_2EtN	98 (Yb) (de=82%)	211
1e			4Å MS	82 (Sc) (de=84%)	69
1f			4Å MS	45 (Sc) (de=40%)	69
1g			4Å MS	1 (Sc) (de=62%)	69
2			4Å MS + 	91 (Yb)	203
3a				96 (Yb) (de=98%)	204
3b				83% without MS -96 (Yb)with MS	205

Table 4. (Continued)

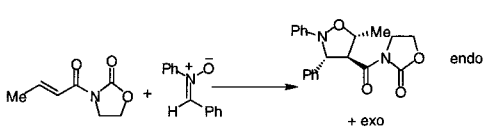
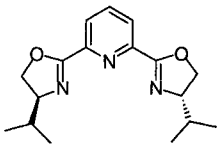
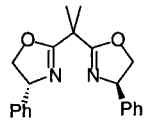
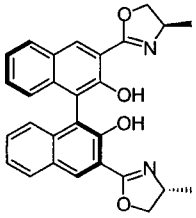
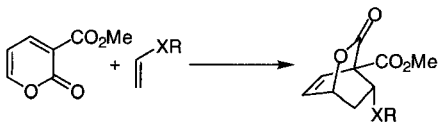
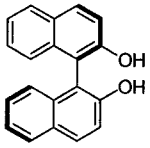
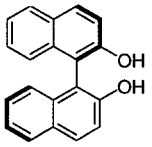
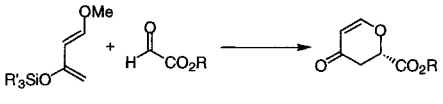
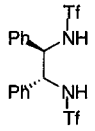
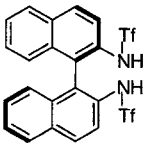
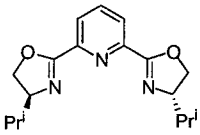
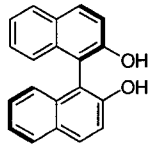
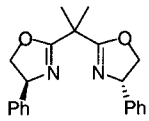
Entry	Reaction	Chiral ligand	Other additive	Max. ee achieved (Ln)/%	Reference
3c				69 (Yb) (de=84%)	66
3d				0	66
3e				83 (Sc) (de=84%)	210
4			$^{i}Pr_2EtN$	96 (Yb) (40% without added amine)	206,207,208
5			Ph_2BnN	80 (Yb)	209
6a				42 (Yb) 54 (Y)	214
6b				5 (Y)	214
6c				60 (Yb) 6 (La)	212
6d				14 (Yb)	212
6e				17 (Yb)	212

Table 4. (Continued)

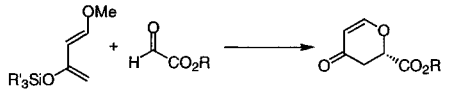
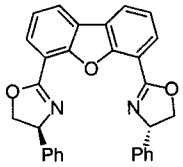
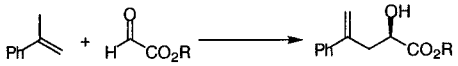
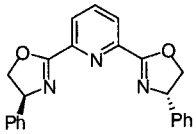
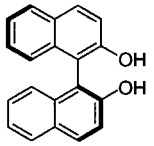
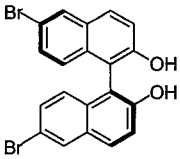
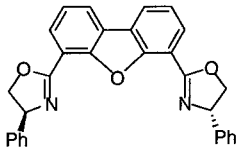
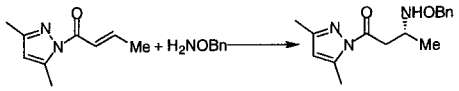
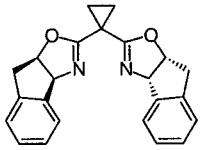
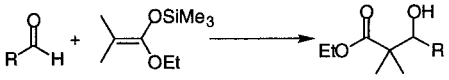
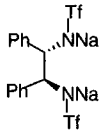
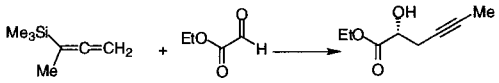
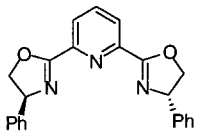
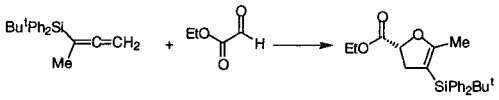
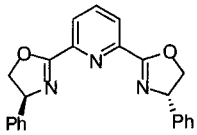
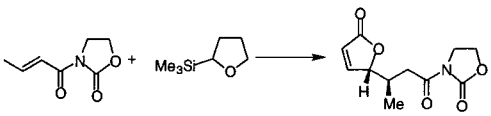
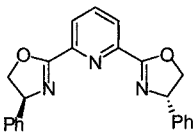
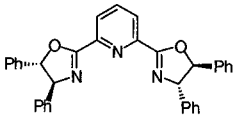
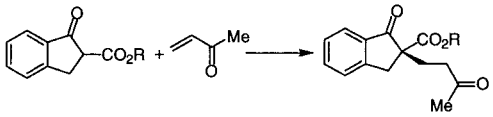
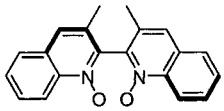
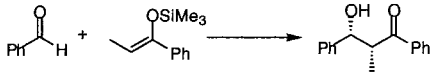
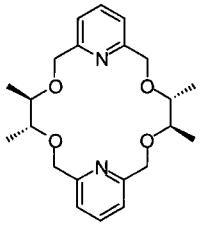
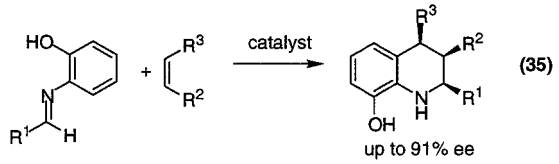
Entry	Reaction	Chiral ligand	Other additive	Max. ee achieved (Ln)/%	Reference
6f				<1 (Yb)	212
7a				50 (Yb)	213
7b				12 (Yb)	261
7c				38 (Yb)	261
7d				1 (Yb)	213
8				59 (Y) 41 (Yb)	262
9				47 (La) 40 (Eu) 33 (Yb)	215
10				98 (Sc)	71
11				94 (Sc)	71
12a				63 (La) 10 (Sc)	70
12b				99 (La) 83 (Sc)	70

Table 4. (Continued)

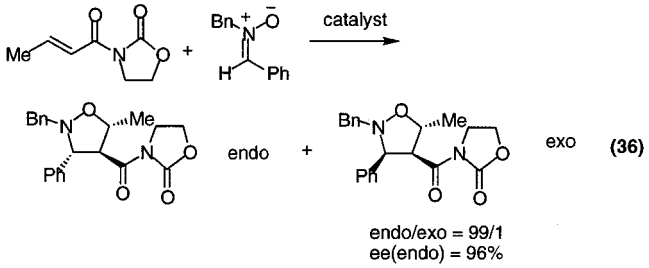
Entry	Reaction	Chiral ligand	Other additive	Max. ee achieved (Ln)/%	Reference
13				80 (Sc)	217
14				82 (Ce) (de=86%) 7 (Y) (de=12%)	107

ylpyridine, which can block any interaction between DBU and the phenolic OH of the imine substrate.[203]



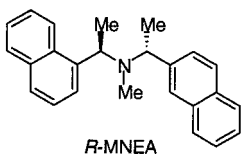
(35)

Excellent diastereoselectivies for the 1,3-dipolar cycloaddition reaction 36 (Table 4, entries 3a,b) were obtained when the catalyst was prepared with any one of several bases; however, the ee was very dependent on choice of base. Use of Et_3N resulted in



(36)

an ee of 63%; this was increased to 96% when *R*-MNEA **122** was used in combination with *S*-binaphthol. Use of *S*-MNEA (i.e., heterochiral catalyst) reduced the ee to 62%, but the sense of the chiral induction was unchanged.[204] The sense of the chiral induction did however depend on the presence of molecular sieves in the reaction medium, although in the absence of molecular sieves the absolute value of the ee was slightly reduced (from 96% to 83%) (Table 4, entry 3b).[205]



R-MNEA

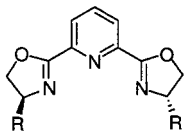
122

The $Yb(OTf)_3$/binaphthol/bulky amine catalyst system pioneered by Kobayashi has also been applied very successfully by Marko to inverse electron demand Diels–Alder reactions (Table 4, entry 4)[206–208] and by Hou to desymmetric ring opening of *meso* epoxides with anilines (Table 4, entry 5).[209]

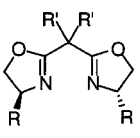
In the absence of base additives binaphthol is much less effective as a chiral ligand (Table 3, entries 6d, 7c, 12c), although the introduction of bulky oxazoline substituents into the 3 and 3′ positions of the binaphthol has resulted in good enantioselectivity for the 1,3-dipolar cycloaddition reaction (Table 3, entry 3c).[210] Another variation on the binaphthol theme is the bis(acylamino)binaphthyl ligand which has been used in combination with amine additive in the Diels–Alder reaction (Table 3, entry 1d).[211]

2. $Ln(OTf)_3$ and $LnCl_3$ Catalysts Containing Bis(oxazoline) Ligands

Chiral $Ln(OTf)_3$ catalysts have been prepared by addition of bis(oxazoline) ligands such as pybox **44** or box **123**; the catalysts are normally prepared by reaction of $Ln(OTf)_3$ with 1 equiv of chiral ligand, and there are now two examples of crystallographically characterized mono(pybox) complexes of $Ln(OTf)_3$ (see section III.B). The pybox ligand has been used very successfully with $Sc(OTf)_3$ for the Diels–Alder reaction (Table 4, entry 1e)[69] and the enantioselective syntheses of homopropargylic alcohols (Table 4, entry 10**)** and dihydrofurans (Table 4, entry 11),[71] with $Yb(OTf)_3$ for the 1,3-dipolar cycloaddition reaction (Table 4, entry 3d)[66] and the hetero-Diels–Alder reaction (Table 4, entry 6c),[212] and with $La(OTf)_3$ for the enantioselective Mukaiyama–Michael reaction (Table 4, entries 12a**,**b).[70] The glyoxylate ene reaction is catalyzed with moderate enantioselectivity by $Yb(OTf)_3$/pybox (Table 4, entry 7a).[213]



44

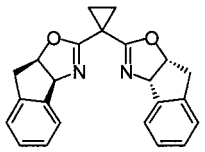


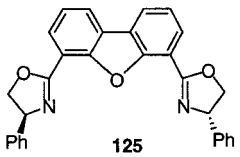
123

In almost all cases the best ee's are obtained with the smaller later Ln^{3+} or indeed with Sc^{3+} where a single pybox ligand would be expected to be most effective in defining a chiral binding site, and many

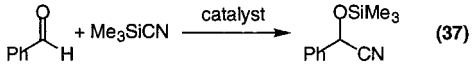
of the most effective reactions involve chelating substrates. The results reported in Table 4, entries 12a,b, are an exception to this general observation: higher ee's are observed for $La(OTf)_3$ than for $Sc(OTf)_3$.

In contrast to the success of the pybox ligand, box ligands **123**, which have been very successful in transition-metal catalysis, generally fail miserably with lanthanide catalysts (Table 4, entries 1g, 3d, 6e). This is probably because they are too small to define an effective chiral binding site at the Ln atom; the most effective box ligand is the dibenzo box **124** as demonstrated in the conjugate addition reaction (Table 4, entry 8). The oxazoline-substituted dibenzofuran ligand **125** was also ineffective (Table 4, entry 7d), probably because it is sterically unsuited to act as a tridentate ligand.



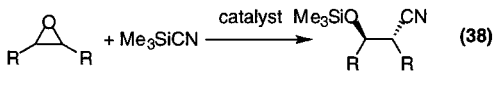


Pybox ligands have also been used in conjunction with $LnCl_3$. For example, enantioselective silylcyanation of aldehydes (reaction **37)** is catalyzed by pybox complexes derived from $LnCl_3$.



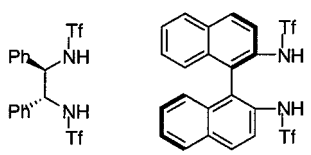
Enantiomeric excesses of up to 89% are obtained for reaction **25** with 5 mol % of a catalyst prepared from $YbCl_3$ and 2 equiv of Ph-pybox **44**. Pr^i-pybox gives somewhat poorer enantioselectivity than Ph-pybox, and the more sterically demanding Bu^t-pybox gives only 14% ee for the silylcyanation of PhCHO. Although the identity of the actual catalyst has not been established, it has been shown that an authentic, characterized sample of $[YbCl_3(pybox)_2]$ catalyzes reaction 37 with exactly the same results as the in situ prepared catalyst.[67]

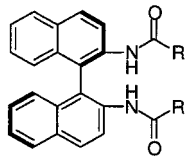
The enantioselective ring opening of *meso* epoxides with Me_3SiCN (reaction 38) is also catalyzed by $YbCl_3$/pybox catalysts with ee's of up to 92%.[68] In this case the catalyst is prepared from hydrated $YbCl_3$ by addition of 1 equiv of pybox. As reactions 37 and 38 involve silylcyanation, it is likely that the active catalyst is a lanthanide cyanide rather than a chloride.



3. $Ln(OTf)_3$ Catalysts Containing Other Chiral N-Donor Ligands

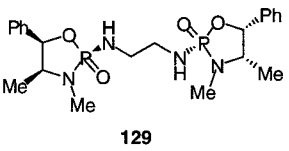
Chiral triflamide ligands **126** and **127** in combination with $Ln(OTf)_3$ have been investigated for catalysis of the hetero-Diels–Alder reaction[214] (Table 4, entries 6a,b) and for the Mukaiyama aldol reaction[215] (Table 4, entry 9) with at best modest enantioselectivity. The binaphthyl-derived ligand **127** gives particularly disappointing results. A much more successful variation on the binaphthyl theme is the bis(acylamino) ligand **128** which, in combination with Pr_2EtN, gives excellent ee's in the Diels–Alder reaction (Table 4, entry 1d).[211]

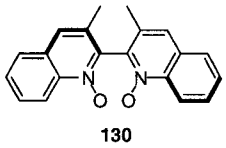




4. $LnCl_3$ and $Ln(OTf)_3$ Catalysts Containing Chiral Phosphine or Pyridine Oxide Ligands

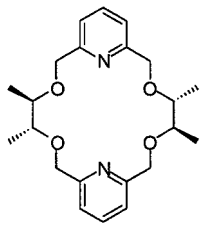
Phosphine and pyridine oxides are long established ligands in lanthanide coordination chemistry, and Ln complexes containing chiral versions of these ligands have been investigated for use in enantioselective catalysis. The complex formed by reaction of 3 equiv of the chelating phosphine oxide **129** with $SmCl_3$ catalyzes the enantioselective silylcyanation of aldehydes (reaction 37**)** with ee's up to 84%.[216] The *N,N′*-dioxide **130** has been used in combination with $Sc(OTf)_3$ to catalyze a Michael reaction (Table 4, entry 13) with ee's up to 80%.[217]





5. $Ln(OTf)_3$ Catalysts Containing a Chiral Macrocycle Ligand

A highly effective enantioselective aldol reaction has been reported using a complex of macrocycle **63** with $Ln(OTf)_3$ (Table 4, entry 14).[107]



The enantioselectivity of this reaction decreases with decreasing Ln radius: the best results are obtained with $[Ce(OTf)_3(\mathbf{63})]$ or $[Pr(OTf)_3(\mathbf{63})]$, and practically zero ee's are obtained for the later lanthanides. The reaction is carried out in mixed H_2O/EtOH solvent, and good diastereo- and enantioselectivities are only obtained in the presence of H_2O. The cavity size of the macrocyclic ligand is well matched to the ionic radius of the early Ln^{3+}, and this probably accounts for the decreasing ee's along the series. $Ln(OTf)_3$ complexes with **63** have not been characterized crystallographically; however, a crystal structure has been obtained for $[Pr(NO_3)_2L][NO_3]$ (see Figure 28), and it is reasonable to expect that the triflate

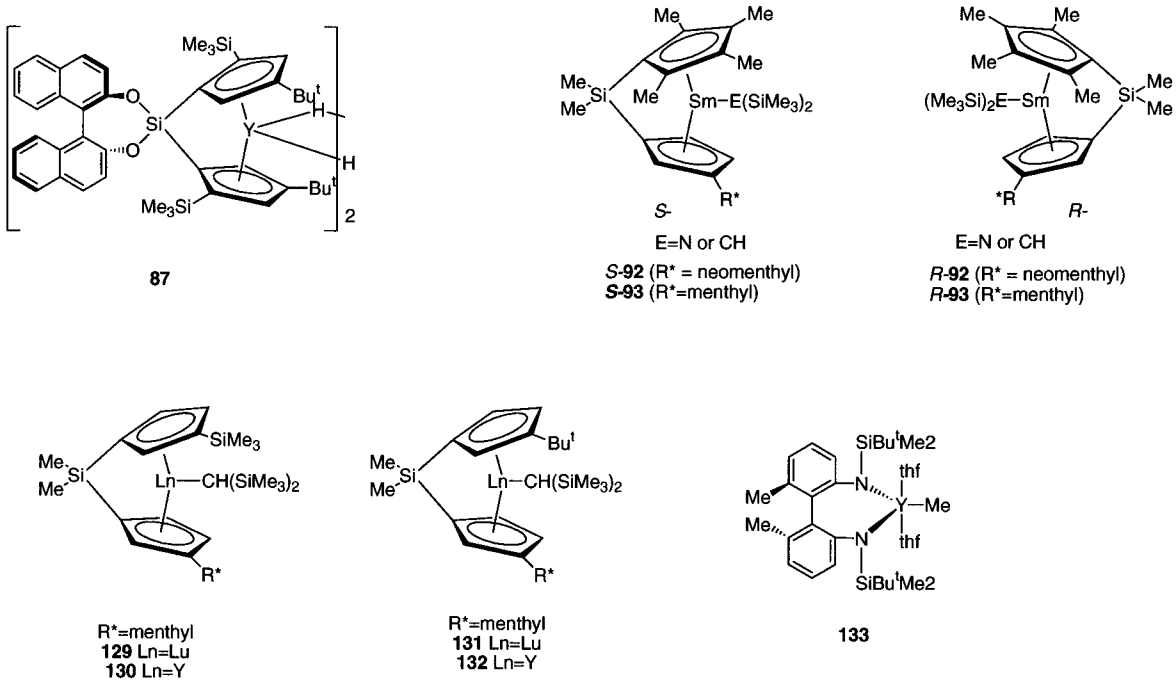


Figure 40. Chiral organolanthanide complexes that have been used to catalyze enantioselective alkene transformations.

complexes would be similar, although in aqueous medium the OTf^- would be expected to be uncoordinated.

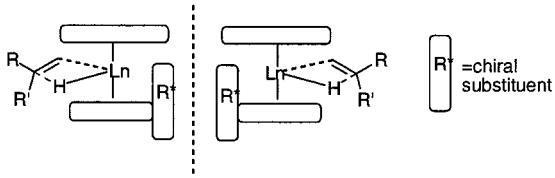
F. Organolanthanide Complexes

Organolanthanide complexes, especially lanthanide bis(cyclopentadienyl)s, catalyze several alkene transformations including hydrogenation, hydrosilylation, hydroamination, and polymerization. The lability often associated with lanthanide−ligand bonds means that these catalysts can show very high activities and turnover rates. The synthesis of chiral lanthanide bis(cyclopentadienyl)s has made enantioselective versions of these important transformations into a reality. Because of the large size of the lanthanide ions and the nonrigid nature of many of their complexes, it is a significant challenge to synthesize complexes that have a sufficiently well-defined chiral binding site to be effective.

1. Alkene Transformations

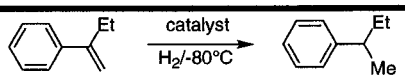
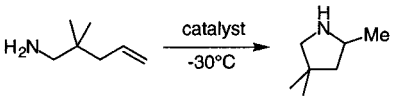
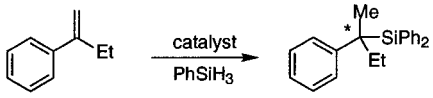
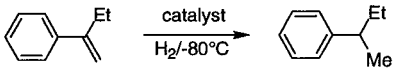
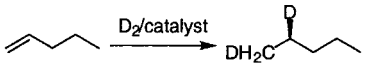
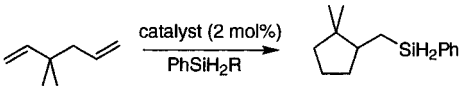
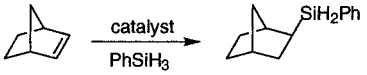
The chiral complexes shown in Figure 40 have all been shown to catalyze stereospecific alkene transformations; these reactions are summarized in Table 5.

The chiral complexes **92** and **93** (see section VII.B) were designed to provide a rigid chiral binding site at Ln and to be readily isolable in enantiomerically pure form. The chiral binding site, which provides lateral/transverse substrate enantioface discrimination, can be represented schematically as shown below.[218]



The alkyl complexes **92** and **93** (E = CH) were first used to catalyze alkene hydrogenation in 1992.[218] The active catalyst is a hydride complex, generated in situ by hydrogenolysis of the Ln−alkyl bond, and the enantioselective step in the catalytic cycle is the irreversible insertion of alkene into the Ln−H bond. In the hydrogenation of 2-ethyl-but-1-ene (Table 5, entries 1a−d**)**, the *R* catalyst is found be selective for the *R*-product and the *S*-catalyst for the *S*-product. The *R*-neomenthyl and *S*-menthyl catalysts give much better enantioselectivity than their *S*-neomenthyl and *R*-menthyl diastereomers. Silylamide or alkyl complexes can be used as precatalysts for the enantioselective hydroamination/cyclization reaction (Table 5, entries 2a−d);[219] the $CH(SiMe_3)_2$ or $N(SiMe_3)_2$ groups are rapidly displaced via protonolysis by the amine group of the substrate. Surprisingly, in the hydroamination/cyclization reaction, the absolute configuration of the product is almost insensitive to the optical purity of the precatalyst, depending only (within experimental error) on the chiral substituent R* (menthyl or neomenthyl). This observation is explained by a rapid epimerization of the catalyst in the presence of an excess of amine so that epimer ratios of 80:20 *R*:*S* (neomenthyl catalyst) and 95:5 *S*:*R* (menthyl catalyst) are established.[220] One example of enantioselective alkene hydrosilylation by these catalysts has been reported (Table 5, entries 3a,b).[221]

Table 5. Alkene Transformations Catalyzed by Chiral Organolanthanide Complexes

Entry	Reaction	Catalyst	Ee/%	Ref
1a		*S/R*-**93** (E=CH)	96 (*S*)	218,220
1b		*R*-**93** (E=CH)	27 (*R*)	
1c		*R*-**92** (E=CH)	71 (*R*)	
1d		*S*-**92** (E=CH)	19 (*S*)	
2a		*S*-**93** (E=N)	72 (*R*)	220
2b		*R*-**93** (E=N)	60 (*R*)	
2c		*S*-**92** (E=N)	55 (*S*)	
2d		*R*-**92** (E=N or CH)	58 (*S*)	
3a		*R*-**93** (E=CH)	68	221
3b		*S*-**93** (E=CH)	65	
4a		**129**	45 (*S*)	223
4b		**130**	28 (*S*)	
4c		**132**	26	222
5a		**132**	61	222
5b		**131**	63	
6		**87**	50	263
7		**133**	90	57

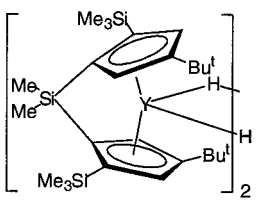
The less sterically hindered complexes **131** and **132**[222] and **129** and **130**,[223] which exist in the pseudo-*meso* configuration, have also been investigated for activity in enantioselective hydrogenation. Enantioseletivities for hydrogenation of 2-phenyl-but-1-ene are only modest (Table 5, entries 4a−c); however, deuteration of 1-pentene gives significantly better results (Table 5, entries 5a,b).

Alkene insertion into the Y−H bond of **87** proceeds with only 34% ee, and so it was recognized that highly enantioselective catalysis of alkene hydrosilylation would be unlikely with this catalyst.[224] However, the cyclization−hydrosilylation of α,ω-dienes involves an alkene insertion into a Y−C bond in the enantioselective step and should be more amenable to catalysis by **87**. An ee of 50% has been achieved in the best case (Table 5, entry 6).

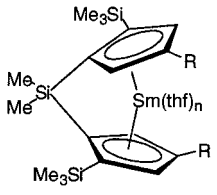
There is just one report of enantioselective alkene hydrosilylation by a Ln complex with non-Cp ancillary ligation. The C_2-symmetric bis(silylamido) complex **133** catalyzes the hydrosilylation of norbornene with 90% ee (Table 5, entry 7); reactions of other substrates have not been reported.[57]

2. Polymerization Reactions

Stereospecific alkene polymerization does not require enantiomerically pure catalysts, and highly *iso*-specific alkene polymerization has been catalyzed by the C_2-symmetric racemic complexes **134**[139] and **135**.[225]



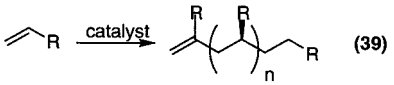
134



135

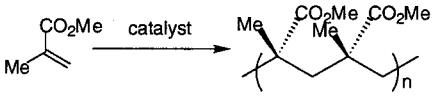
R=Bu^t n=2
R=Bu^{t}Me$_2$Si n=3

112 was the first *iso*-specific single-component catalyst for Ziegler−Natta polymerization (reaction 39).



(39)

The enantiomerically pure C_1-symmetric alkyl complexes **92** and **93** (E=CH) have been investigated as catalysts for methyl methacrylate polymerization (reaction 40**)**. *R*-**92** (Ln = La; E = N) gives high selectivity for isotactic polymer, whereas catalysts **93** bearing the menthyl chiral auxiliary produce syndiotactic polymers with similar stereoregularity to that obtained with achiral catalyst.[226]



(40)

X. Chiral Lanthanide Reagents

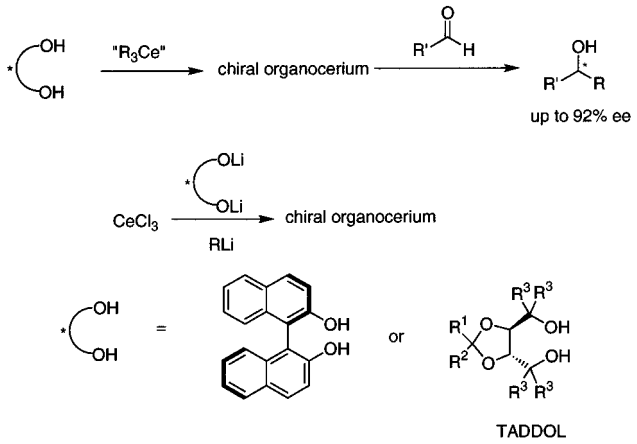
A. Chiral Alkoxide Complexes in Enantioselective Alkyl Addition

In 1984 organocerium reagents were first recognized as mild and highly selective reagents for alkyl addition to carbonyls.[227] The oxophilicity of the Ce and the reduced basicity of the alkyl species are crucial to the effectiveness of these reagents. Ce was the lanthanide of choice simply because of its high abundance and consequent low cost. The organocerium reagents are generated by reaction of CeX_3 (X = halogen) with RLi in an ethereal solvent. Although their structures are not known, their reactivity is distinctly different from that of the parent RLi, and it has been suggested by Denmark that they have the composition $Li_3CeCl_3R_3$.[228] Chiral organocerium reagents incorporating chiral diols can be prepared as shown in Scheme 5. These chiral organocerium reagents mediate enantioselective alkyl addition to a range of aldehydes. The most effective diols were found to be binaphthol[23] and TADDOLs.[229]

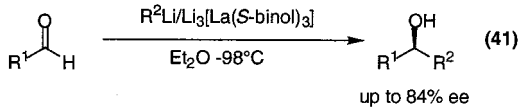
The highest ee's are obtained when 3 equiv of diol is used per Ce.[229,230] Substituent effects in the TADDOL reagent were investigated, and it was found that for addition of Bu^n to aldehydes, the best results were obtained with $R^1 = R^2 = Me$ and $R^3 = Ph$; the more sterically demanding TADDOL with $R^3 = 3,5\text{-}Me_2Ph$ resulted in very poor enantioselectivity. The nature of the substituents remote from the Ce were also found to be important, and the C_1-symmetric TADDOL with $R^1 = Ph$, $R^2 = H$, and $R^3 = Ph$ gave very low ee's.[231]

The observation that the most effective reagents were those prepared from 3 equiv of diol per Ce suggested that these reagents may have structures analogous to the Shibasaki heterometallic alkali-metal lanthanide binaphtholates $M_3[Ln(binol)_3(H_2O)]$ but without the acidic coordinated H_2O, which would be incompatible with a strongly basic organolanthanide species. Anhydrous $M_3[Ln(binol)_3]$ complexes have been prepared from lanthanide tris(silylamide)s by as described in section II.A.3.

Scheme 5



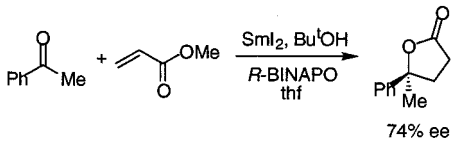
These complexes have been characterized by X-ray diffraction, and their structures are discussed in section II.A.4.[25] $[Li(thf)_2]_3[Ln(binol)_3]$ have been found to be effective reagents for enantioselective alkyl addition to a range of aldehydes (reaction 41**)**. There is a strong dependence on Ln ionic radius, with the best enantioselectivity observed for La and almost zero ee for Yb.[24]



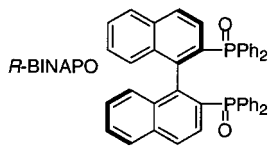
(41)

B. Chiral Sm(II) Reagents

The use of Sm(II) as a selective one-electron reducing agent in organic synthesis is well established. There is, however, relatively little published work on chiral modifications of Sm(II) reagents. The addition of the chiral phosphine oxide *R*-BINAPO to SmI_2 gives a chiral one-electron reducing agent that allows enantioselective addition of ketones to α,β-unsaturated esters to give γ-butyrolactones (reaction 42).[232]



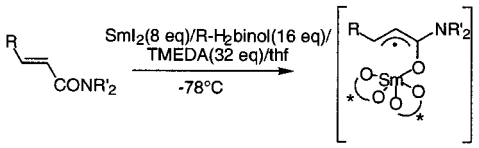
(42)

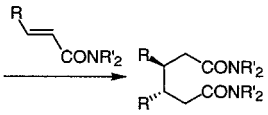


Diastereo- and enantioselective hydrodimerization of β-monosubstituted acrylic acid amides can be achieved using a combination of SmI_2 with binaphthol as shown in reaction 43. A chiral bis(binaphthol) complex of Sm is proposed as the enantioselective reagent; it must be used in very large excess as it gradually decomposes at −78 °C.[233]

Enantioselective protonation of Sm enolates (reactions 44 and 45) using chiral proton sources has been investigated by Mikami and by Takeuchi.[234,235]

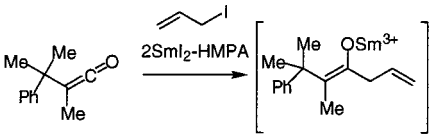
The most effective chiral proton sources are found to be multidentate alcohols such as **136**, **137**, and **138**, which are able to form stable chelate rings on

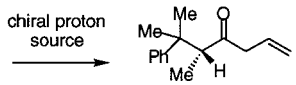




(43)

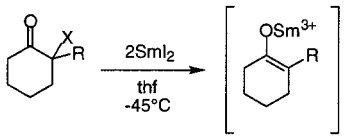
up to 70% yield
71% ee

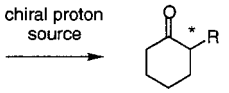




(44)

up to 93% ee

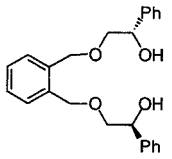




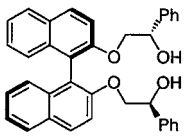
(45)

up to 94% ee

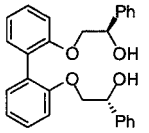
coordination to Sm^{3+}. Tetradentate alcohols were found to be more effective than the more sterically demanding pentadentate ones such as **139**.



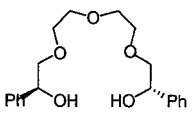
136



137



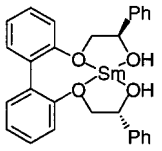
138



139

Chiral Sm(III) alcohol complexes such as **140** have been proposed as the reactive protonating agents.[49] The structures of these complexes would be expected to resemble those of ligands **30** and **31** as described in section II.B.I. Conformational chirality in the chelate rings can either be locked into the ligand as in the binaphthol derived **137** or induced as in the equally effective biphenyl ligand **138**.

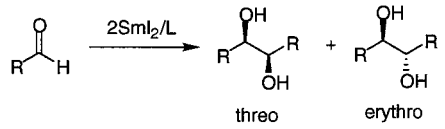
Use of catalytic quantities of the chiral proton source has been achieved for reaction 44 with ee's up to 93%. In this case the achiral alcohol Ph_3COH was used to regenerate the chiral proton source.[236] Reaction 44 has also been carried out using catalytic



140

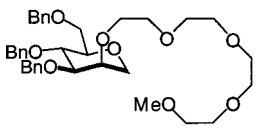
chiral proton source in fluorous biphasic media with ee's of up to 90%.[237]

Sm(II) is well established as a reagent for the pinacol coupling reaction 46. There has been some

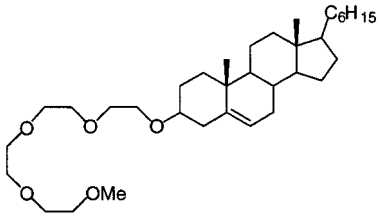


(46)

investigation of the effect on diastereoselectivity of adding multidentate donors to the Sm(II). Tetraglyme, an achiral pentadentate ligand, can increase diastereoselectivity in this reaction to 14:1 (threo: erythro) for the coupling of tetrahydrobenzaldehyde;[238] however, the diastereoselectivity is very dependent on the aldehyde: coupling of benzaldehyde by SmI_2/tetraglyme results in 1:5.9 threo:erythro. Addition of the chiral tetraglyme analogues **141** and **142** to SmI_2 resulted in a slight decrease in the threo: erythro ratio, and no enantioselectivity was observed.[239]



141



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XI. Conclusions

The lanthanide elements have unique reactivity and magnetic and optical properties which are fundamental to most of their applications. This review has surveyed chiral lanthanide complexes and some of the applications that combine the unique properties of the lanthanides with a chiral coordination sphere. The combination of magnetic properties with a chiral coordination sphere resulted in the first application of chiral lanthanide complexes. Chiral NMR shift reagents were first developed in the 1970s and are now indispensable tools in the determination of enantiomeric purity of a range of substrates. The optical properties of chiral lanthanide complexes have been probed by circularly polarized luminescence spectroscopy, but as this technique is not widely available, general applications are still some way in the future. Applications in enantioselective catalysis

have developed from very modest beginnings in the early 1980s to the stage where many reactions can now be catalyzed with high ee's (>90%) using low catalyst loadings and convenient experimental conditions. However, the factors that enhance catalytic activity in Ln complexes (e.g., labile Ln−ligand bonds, flexible coordination geometry) make it very difficult to define an effective chiral binding site for the substrate. Consequently the number of really effective catalyst systems is limited; binaphthol and pybox are the most consistently useful ligands. The early promise of chiral organolanthanide complexes in enantioselective catalysis has not yet been fulfilled: catalytic activities are high, but high ee's are obtained in only a limited number of reactions and with a very small number of catalysts. Several groups worldwide are working on the synthesis of new chiral lanthanide complexes for catalysis, but effective chiral ligand sets are still proving elusive, and this area presents significant challenges for some time to come.

XII. References

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