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Defining effective chiral binding sites at lanthanides—highly enantioselective reagents and catalysts from binaphtholate and pybox ligands

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Abstract

This paper reviews our work with enantioselective lanthanide reagents and catalysts for organic synthesis. Heterometallic reagents $M_3[Ln(binol)_3]$ (M = Li; Ln = lanthanide; H_2binol = binaphthol) mediate the addition of RLi to aldehydes with ee's of up to 84%. Structural studies have been carried out where M = Li or Na, Ln = Eu, Y or Yb and with enantiomerically pure or racemic binol. There are important differences in coordination chemistry dependent on the ionic radius of M and Ln. $[LnCl_3(pybox)_2]$ are effective catalysts for the silylcyanation of aldehydes, giving ee's of up to 89% under convenient reaction conditions. Structural studies have been undertaken on $[Ln(OTf)_3(Pr^i\text{–pybox})_2]$ for Ln = La, Eu or Yb.

Keywords: Binaphthol; Catalysis; Cyanohydrin; Enantioselective synthesis; Lanthanide; Pybox

1. Introduction

The lanthanide elements have now become important components of the synthetic organic chemist's toolkit. In 1984 organocerium reagents were first recognized as mild and highly selective reagents for alkyl addition to carbonyls [1], where the oxophilicity of the Ce and the reduced basicity of the alkyl species are crucial to the effectiveness of the 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 $Li_3CeCl_3R_3$ [2]. The mild Lewis acidity of lanthanide triflates $Ln(OTf)_3$ ($OTf = CF_3SO_3$) has been exploited in their use as selective Lewis acid catalysts showing high turnover in a range of useful transformations [3,4]. As well as the practical attractions of relatively low cost, high abundance and low toxicity, the lanthanide elements have chemical features which make them attractive as components of reagents and catalysts for organic synthesis: their oxophilicity combined with lability of the Ln–O bond means that they show mild Lewis acidity combined with rapid dissociation of product after reaction of the substrate. This means that turnover rates can be much higher than for traditional Lewis acids such as BF_3 or $AlCl_3$, where stoichiometric amounts are often required. The large coordination sphere and flexible coordination geometry typical of lanthanide complexes can also be advantageous, allowing coordination of a wide range of substrates and thus being applicable to a potentially wider range of reactions. In addition, the steady decrease in ionic radius on traversing the lanthanide series allows fine-tuning of activity and selectivity of reagents and catalysts.

An important goal for many synthetic organic chemists is the synthesis of enantiomerically pure molecules. Enantioselective catalysis, which requires only a substoichiometric quantity of chiral auxilliary, is especially attractive but requires a catalyst with a well-defined chiral binding site for the substrate. However, features of lanthanide chemistry which enhance reactiv-

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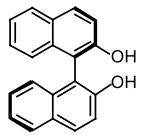
ity (e.g. labile Ln-to-ligand bonds) make it more difficult to prepare enantioselective catalysts and reagents. In this paper we review some of our work with chiral lanthanide complexes which has resulted in a highly enantioselective reagent for alkyl addition to aldehydes and a highly enantioselective catalyst for cyanohydrin synthesis.

2. Enantioselective organolanthanide reagents

2.1. In situ generated reagents

Imamoto's alkyl cerium(III) reagents show remarkable selectivity in their addition reactions to carbonyls, and our work in this area began with the modification of organocerium reagents using chiral diols such as *R*-binaphthol (H_2binol) (**1**) and TADDOLs (α,α,α′,α′-tetraaryl-1,3-dioxolan-4,5-dimethanols) (**2**).



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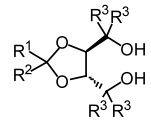
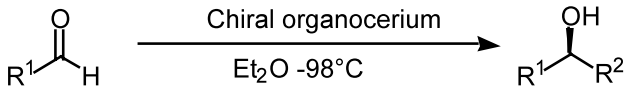


2

The chiral reagents were generated in situ, as shown in reaction (1) below:

$$LnCl_3 + 3RLi + diol \xrightarrow{Et_2O} \text{'chiral organolanthanide'} \quad (1)$$

These chiral organolanthanide reagents were effective in the enantioselective alkyl addition to aldehydes as shown in reaction (2).

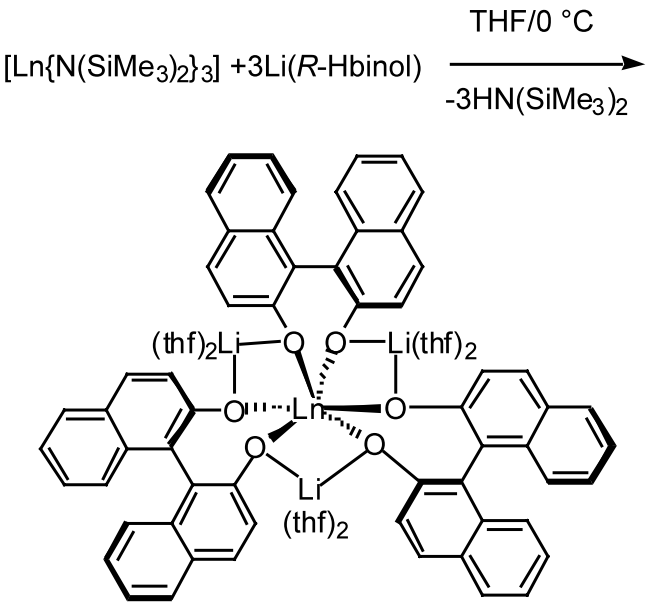


up to 94% ee (2)

We found that the optimum enantioselectivities were obtained when three equivalents of TADDOL [5] or binaphthol [6] was used, along with sufficient alkyllithium to deprotonate the additional diol. While we were involved in this work, Shibasaki was independently investigating the use of lanthanide binaphtholate catalysts. When the Shibasaki catalysts were shown to be heterometallic alkali-metal lanthanide *tris*(binaphtholate)s with the general formula $M_3[Ln(binol)_3(H_2O)]$ [7], it occurred to us that our reagents might well have a similar structure. We therefore set about developing a rational synthesis of *anhydrous* analogues of Shibasaki's catalysts, which would allow us to investigate systematically the effect the alkali metal and the lanthanide radius on structure and reactivity. Clearly the presence of the acidic coordinated H_2O in the Shibasaki catalysts would be incompatible with an organolanthanide species.

2.2. Preparation of $M_3[Ln(binol)_3]$

We chose lanthanide *tris*(silylamides) [Ln{N-$(SiMe_3)_2$}] as soluble, anhydrous, alkali metal- and halide-free precursors to binaphtholate complexes. Reaction of three equivalents of LiHbinol to a THF solution of [Ln{N$(SiMe_3)_2$}] at 0 °C resulted in quantitative formation of the desired product as shown in reaction (3).



(3)

2.3. Enantioselective alkyl addition reactions mediated by $[Li(THF)_2]_3[Ln(binol)_3]$

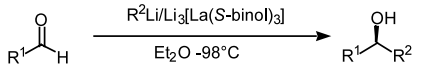
Alkylating agents were generated by addition of RLi (one equivalent) to an Et_2O solution of $[Li(THF)_2]_3[Ln(binol)_3]$ at −78 °C. After ageing for 1 h at this temperature the reagent was cooled to −98 °C and an Et_2O solution of aldehyde was added over a period of 2 h. We investigated the effect of Ln on the enantioselectivity: there was a dramatic decrease in the % ee for addition of MeLi to PhCHO from La (84%) to Yb (3%) demonstrating the importance of Ln ionic radius on this reaction. A range of aldehydes was investigated, and some of our results are summarized in Table 1, illustrating the wide scope of the reaction. We have so far been unable to achieve useful results in additions to ketones.

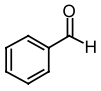
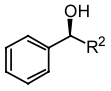
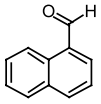
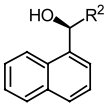
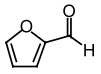
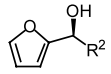
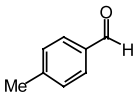
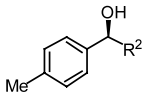
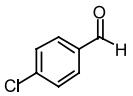
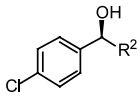
2.4. Structural studies of $M_3[Ln(binol)_3]$

Homochiral $M_3[Ln(binol)_3]$ complexes have been characterized crystallographically for M = Li, Ln = Eu, Y, Yb and for M = Na, Ln = Y, Yb [8]. Unfortunately crystals of $[Li(THF)_2]_3[La(binol)_3]$ always broke down with loss of solvent and so we were unable to determine

its structure crystallographically. The structure of $[Li(THF)_2]_3[Y(R\text{-binol})_3]$ is shown in Fig. 1; the main features of other homochiral $Li_3[Ln(binol)_3]$ complexes are similar. We found that in all of the $Li_3[Ln(binol)_3]$ complexes, the three Li atoms and the Ln atom are either exactly coplanar (crystallographically imposed for Ln = Y or Yb) or close to coplanar (Ln = Eu). However, where M = Na, the complex is pyramidalized, with the Ln atom lying ca. 0.4 Å out of the plane of the Na atoms. This situation is similar to that observed in the Shibasaki $M_3[Ln(binol)_3(H_2O)]$ complexes, where the pyramidalization can be ascribed at least in part to the coordination of one molecule of H_2O along C_3 axis of the complexes. The structures of the M_3LnO_6 cores of $[Li(THF)_2]_3[Y(R\text{-binol})_3]$ and $[Na(THF)_2]_3[Y(R\text{-binol})_3]$ are shown for comparison in Fig. 2(a–b). However, NMR studies show that all the complexes (M = Li or Na) adopt D_3 symmetry in solution, even down to 173 K.

Table 1
Enantioselective alkyl addition to aldehydes mediated by $Li_3[La(binol)_3]$



Substrate	Product	% ee (R^2=Me)	% ee (R^2=Bu^n)
		84	74
		67	67
		70	
		62	
		33	

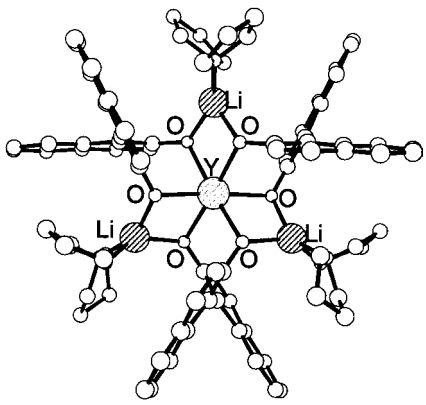


Fig. 1. Structure of $[Li(THF)_2]_3[Y(R\text{-binol})_3]$.

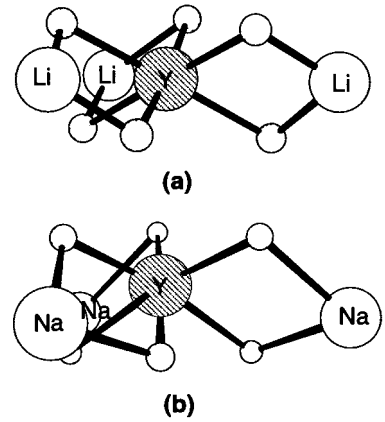


Fig. 2. Views of the M_3LnO_6 cores of: (a) $[Li(THF)_2]_3[Y(R\text{-binol})_3]$; and (b) $[Na(THF)_2]_3[Y(R\text{-binol})_3]$.

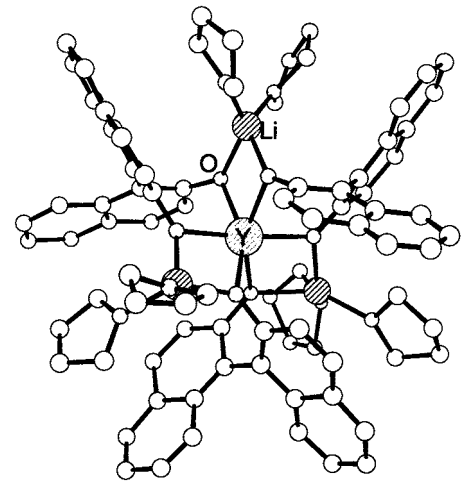


Fig. 3. Structure of $[Li(THF)_2]_3[Y(R\text{-binol})_2(S\text{-binol})]$.

In developing reagents for enantioselective synthesis, it is of more immediate interest to use enantiomerically pure rather than racemic binaphthol. However, we have also carried out some studies using racemic binaphthol, with some perhaps surprising results. Reaction of $[Y\{N(SiMe_3)_2\}_3]$ with three equivalents of *rac*-LiHbinol resulted in formation of a single product. The aromatic region of the ^{1}H-NMR spectrum showed a doublet at an unexpectedly high field (δ 5.82), which indicated that the structure was very different from that of $[Li(THF)_2]_3[Y(R\text{-binol})_3]$. X-ray diffraction showed the '*rac*' compound to consist of $[Li(THF)_2]_3[Y(R\text{-binol})_2(S\text{-binol})]$ and its *RSS* enantiomer which crystallize together in a centrosymmetric space group. The

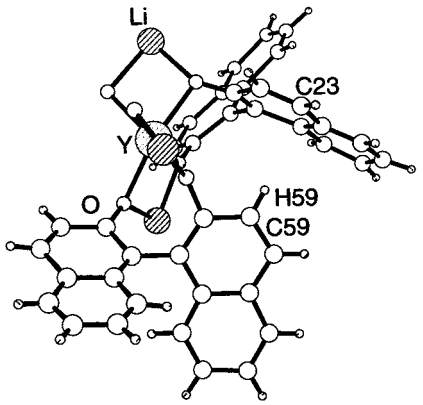


Fig. 4. The close approach of H59 to C23 in $[Li(THF)_2]_3[Y(R\text{-binol})_2(S\text{-binol})]$.

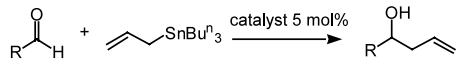
structure of the *RRS* enantiomer is shown in Fig. 3. The anomalous ^{1}H-NMR spectrum of this complex is accounted for by the close approach of H59 of the unique binol ligand to the π-system of the neighbouring naphthyl ring as shown in Fig. 4.

The selective formation of *RRS* and *SSR* $M_3[Ln(binol)_3]$ from racemic binol is very sensitive to ionic radius, both of M and of Ln. Reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with three equivalents of *rac*-NaHbinol resulted in formation of a racemic mixture of *RRR*- and *SSS*-$Na_3[Ln(binol)_3]$ (Ln = Y) or a mixture of *RRR*-/*SSS*- and *RRS*-/*SSR*-$Na_3[Ln(binol)_3]$ in the ratio of 3:1 (Ln = Yb). *RRS*- and *SSR*-$M_3[Ln(binol)_3]$ are a new type of chiral $M_3[Ln(binol)_3]$ complex, and their ready formation suggests that enantioselective catalysts and reagents may be available from binaphthol of low optical purity.

3. Chiral lanthanide Lewis acid catalysts

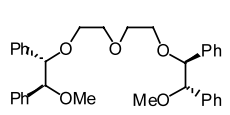
3.1. Lanthanide triflates with chiral O-donor ligands

Our interest in lanthanide triflates began in 1994 with our observation that $Yb(OTf)_3$ is an excellent catalyst for the allylation of aldehydes with allyltributylstannane (reaction (4)) [9].



(4)

We have subsequently been interested in modifying $Ln(OTf)_3$ with chiral ligands. Preliminary investigations indicated that the coordination of polyethyleneglycols $HO(CH_2CH_2O)_nH$ ($n = 2$, 3 or 4) to $Ln(OTf)_3$ gave easy-to-handle catalysts which still showed reasonable activity in the allylation reaction, and complexes with polyethers $MeO(CH_2CH_2O)_nMe$ ($n = 2$, 3 or 4) were good catalysts for the Diels Alder reaction [10]. This encouraged us to prepare a series of chiral polyether and polyethyleneglycol ligands e.g. **3** and **4** as a route to chiral lanthanide triflate catalysts [11].



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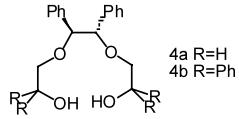

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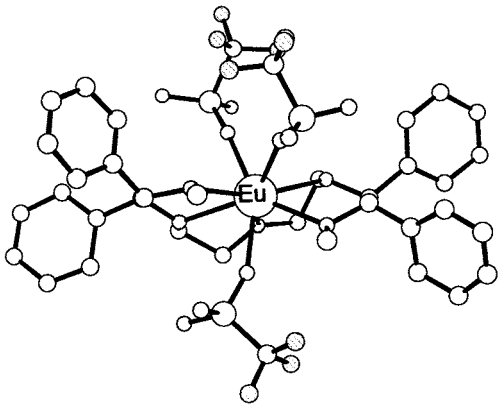
Complexes with the novel ligands **3** and **4a** were prepared, and crystal structure determinations were carried out for $[Eu(OTf)_3(\mathbf{3})]$ [12] and $[Yb(OTf)_3(\mathbf{4})(H_2O)]$ [13]. The structures of these complexes are shown in Figs. 5 and 6.

Disappointingly, catalytic studies with these ligands showed very poor enantioselectivity for both the allylation and Diels–Alder reactions. It is probable that these acyclic ligands are too flexible to define a good chiral binding site for a substrate molecule at Ln.

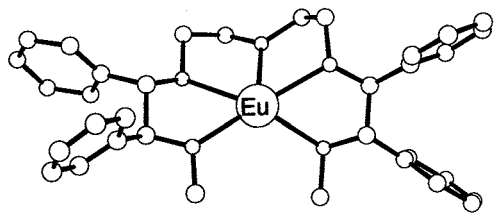
3.2. Lanthanide complexes with pybox ligands

3.2.1. Approaches to enantioselective catalysts for cyanohydrin synthesis

The addition of cyanide ion to aldehydes or ketones generates cyanohydrins as shown in reaction (5).



(a)



(b)

Fig. 5. (a) Structure of $[Eu(OTf)_3(\mathbf{3})]$. (b) View of $[Eu(OTf)_3(\mathbf{3})]$ perpendicular to the EuO_5 'plane' (OTf omitted for clarity).

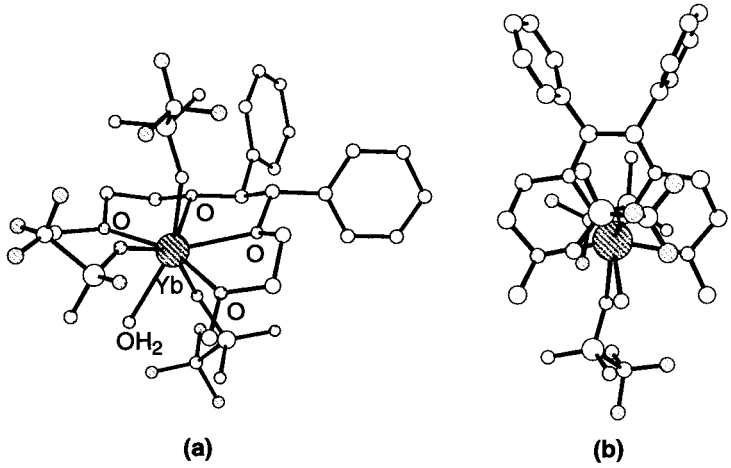
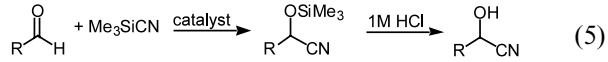


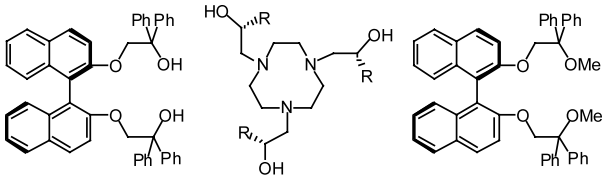
Fig. 6. (a) Structure of $[Yb(OTf)_3(\mathbf{4})(H_2O)]$: (b) View of $[Yb(OTf)_3(\mathbf{4})(H_2O)]$ perpendicular to the YbO_4 'plane' (OTf omitted for clarity).



(5)

The cyanohydrin functional group is an important tool in synthetic organic chemistry as it can be incorporated intact into complex molecules or it may be transformed into a number of other functional groups e.g. α-amino acids, α-chloronitriles, hydroxyaldehydes and acids. Except for those derived from symmetrical ketones where $R = R'$, all cyanohydrins are chiral, and formation of enantiomerically pure cyanohydrins is an important synthetic goal. When we began this work, lanthanide chlorides [14], cyanides [15] and alkoxides [16] had all been reported to catalyze formation of cyanohydrins from aldehydes.

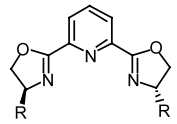
Our first approach was to prepare chiral lanthanide alkoxides using the multidentate alcohols **5** and **6**.



5 **6** **7**

The resulting complexes were effective catalysts for the silylcyanation of aldehydes, but unfortunately the products were racemic in all cases. We have ascribed this to the reaction of coordinated alkoxide with Me_3SiCN to form silylated alcohol, which then dissociates from Ln, along with $Ln(CN)_3$. Acyclic chiral polyethers such as **7** were also ineffective: soluble complexes were formed with $LnCl_3$, but the chiral ligand did not bind strongly enough.

At this point we turned our attention to pybox ligands **8** which have been used successfully with several transition-metal catalyzed enantioselective reactions [17].



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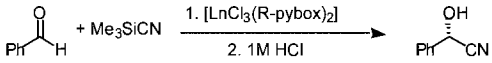
We found that addition of one equivalent of Pr^i–pybox to a THF slurry of $PrCl_3$ led to immediate dissolution of some of the $PrCl_3$, demonstrating that complex formation had occurred. The resulting solution catalyzed the silylcyanation of PhCHO (10 equivalents): the reaction was complete after 16 h at room temperature and the product was isolated in 81% yield with 21% ee. FAB mass spectrometry of the Pr complex formed indicated that it was $[PrCl_3(pybox)_2]$, and in subsequent catalytic reactions we used two equivalents of pybox per Ln. After this promising early result we investigated the effect of Ln^{3+} radius, solvent, and pybox substituent on the reaction. The optimum solvent was found to be MeCN, and a summary of the most important observations is presented in Table 2. As expected, enantioselectivity increased with decreasing ionic radius of Ln^{3+}; a more surprising observation is the reversal in ee between La and the later Ln, which indicates important structural differences as the lanthanide series is traversed. One might have expected that the large Bu^t substituent would give the best ee, but in fact Bu^t–pybox resulted in the worst enantioselectivity. Ph–pybox gave the best enantioselectivity in the silylcyanation of PhCHO, but the more readily available Pr^i–pybox has been used to establish the scope of the reaction. A representative selection of results is summarized in Table 3. The results reported in this table were obtained using 10 mol% of catalyst, but we have recently found that catalyst loadings of 5 mol% can be used without loss of enantioselectivity. Use of hydrated $YbCl_3$ to generate the catalyst results in slightly reduced enantioselectivity [18].

3.2.2. Structural studies of lanthanide pybox complexes

Having established that lanthanide pybox complexes can give highly effective enantioselective catalysts, we embarked on some studies of the complexes. The first fact that we established was that the catalysts for the silylcyanation reaction contain two pybox ligands per Ln: an equimolar mixture of $[LnCl_3(pybox)_2]$ and unreacted $LnCl_3$ was formed on addition of one equivalent of pybox to $LnCl_3$. NMR spectroscopy showed that free and coordinated pybox did not exchange in a CD_3CN solution of $[LnCl_3(pybox)_2]$ containing excess pybox. X-ray quality crystals of $[LnCl_3(pybox)_2]$ have not yet been obtained, but we have found $Ln(OTf)_3$ complexes easier to crystallize. $Ln(OTf)_3$/pybox catalysts have been used in enantioselective 1,3-dipolar cycloaddition reactions [19] and so their structures are of wide interest.

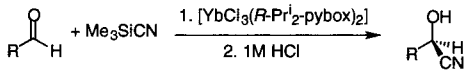
Table 2
Effect of Ln and Pybox substituent on enantioselective hydrocynation of phCHO

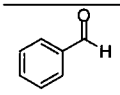
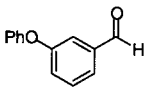
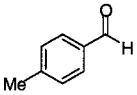
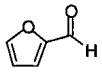
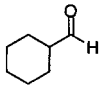
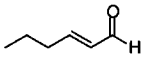


Ln	R	Time (h)	Isolated yield (%)	ee (%)
Y	Pr^i	1	87	67
Y	Ph	1	77	80
Y	CH_2Ph	1	100	60
La	Pr^i	3	96	12 [a]
Eu	Pr^i	16	81	32
Yb	Pr^i	1	94	75
Yb	Ph	0.5	61	89
Yb	Bu^t	3	88	13.8

[a] Reversal of enantioselectivity.

Table 3
Enantioselective addition of Me_3SiCN to aldehydes catalyzed by $[YbCl_3(Pr^i\text{–pybox})_2]$



Aldehyde	Isolated yield/%	Ee/%
	94	75
	98	68
	93	70
	86	67
	86	60
	88	58

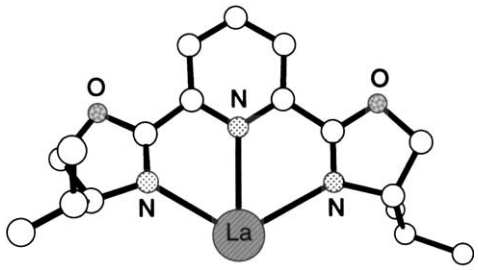


Fig. 7. Structure of the La(*S*-Pr^i–pybox) fragment of $[La(OTf)_3(Pr^i\text{–pybox})_2]$.

We have now obtained preliminary X-ray crystal structures of several $Ln(OTf)_3$ complexes with pybox ligands [20,21]. $[Ln(OTf)_3(R\text{-}Pr^i\text{–pybox})_2]$ is a nine-coordinate complex with two tridentate pybox ligands and all three OTf ions coordinated. Fig. 7 shows the La(Pr^i–pybox) fragment, illustrating how the large La^{3+} ion is accommodated by the pybox ligand. In transition metal complexes, the N1–M–N2 angle is close to 90°; corresponding angles for Ln(Pr^i–pybox) complexes are shown in Table 4.

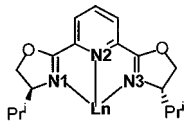
A single pybox ligand is able to define an effective chiral binding site at a transition metal center, but this is not possible with the large Ln ions, where the cooperative effects of two pybox ligands are required. Fig. 8 shows the $La(pybox)_2$ fragment of $[La(OTf)_3(R\text{-}Pr^i\text{–pybox})_2]$, illustrating this effect. The radius of Yb^{3+} is too small to accommodate three OTf ligands as well as two tridentate pybox ligands, and the salt $[Yb(OTf)_2(Pr^i\text{–pybox})_2][OTf]$ is formed on crystallization from THF/Et_2O. Fig. 9 shows the structure of $[Yb(OTf)_2(Pr^i\text{–pybox})_2][OTf]$.

Jacobsen's report of non-linear effects in $YbCl_3$/pybox catalyzed enantioselective opening of epoxides with Me_3SiCN [22] prompted us to investigate the coordination chemistry of Ln with racemic pybox. Our preliminary results indicate that reaction of $Ln(OTf)_3$ with *rac*-Pr^i–pybox gives exclusively *RS*-$[Ln(OTf)_3(pybox)_2]$ for Ln = Eu, and a mixture of mainly *RR*- and *SS*- with a small amount of *RS*-$[Ln(OTf)_3(pybox)_2]$ for Ln = Yb. The structure of the [Eu(*R*-Pr^i–pybox)(*S*-Pr^i–pybox)] fragment of $[Eu(OTf)_2(R\text{-}Pr^i\text{–pybox})(S\text{-}Pr^i\text{–pybox})(H_2O)][OTf]$ is shown in Fig. 10.

4. Conclusions

Despite the considerable difficulties associated with large Ln^{3+} radius and ligand lability we have shown

Table 4
Geometrical data for Ln(pybox)



Ln	N1–Ln–N2 (°)	N1–Ln–N3 (°)	N1–Ln (Å)	N2–Ln (Å)	N3–Ln (Å)
La	60.8	60.6	2.753	2.711	2.686
Eu	62.0	63.7	2.590	2.579	2.502
Yb	65.0	65.0	2.483	2.433	2.487

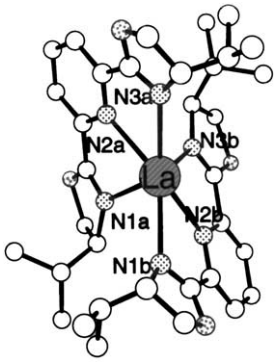


Fig. 8. Structure of [La(OTf)$_3$(*S*-Pr^i–pybox)$_2$] (OTf omitted for clarity).

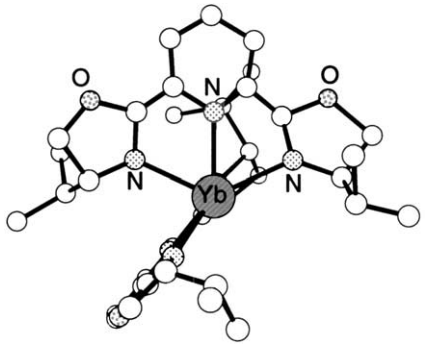


Fig. 9. Structure of [Yb(OTf)$_2$(*R*-Pr^i–pybox)$_2$][OTf] (OTf omitted for clarity).

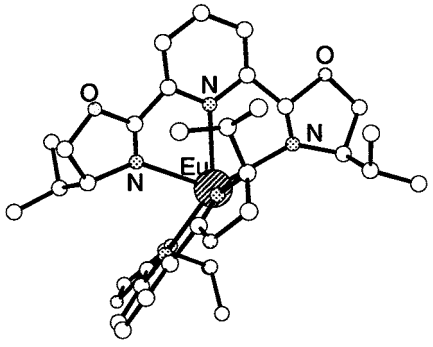


Fig. 10. Structure of [Eu(OTf)$_3$(*S*-Pr^i–pybox)(*R*-Pr^i–pybox)(H$_2$O)] (OTf and H$_2$O omitted for clarity).

that carefully chosen multidentate ligands can define effective chiral binding sites at Ln, resulting in highly enantioselective reagents and catalysts. Small variations in ionic radius as the lanthanide series is traversed can result in significant differences in coordination chemistry and in enantioselectivity of reagents and catalysts.

Acknowledgements

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