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Lanthanide Pybox Complexes as Catalysts for Enantioselective Silylcyanation of Aldehydes

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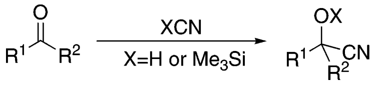
Complexes of lanthanide chlorides with pybox ligands catalyze the enantioselective silylcyanation of aromatic and aliphatic aldehydes with ee's of up to 91% under mild and convenient conditions. Studies of catalysts prepared with pybox ligands of varying enantiomeric purity show no marked nonlinear effects, indicating a monometallic transition state. A mechanism for the catalytic reaction is proposed. Crystal structures of [LnCl$_2$(*S*-Pr^i-pybox)$_2$][LnCl$_4$(*S*-Pr^i-pybox)] (Ln = Eu, Yb) are reported. The structure of the related triflate complex [La(OTf)$_3$(*S*-Pr^i-pybox)$_2$] is also reported. Diastereoselectivity has been observed in the reactions of Ln(OTf)$_3$ with racemic Pr^i-pybox: for Ln = Eu, a heterochiral product containing one *R*- and one *S*-pybox ligand is observed, whereas for Ln = Yb a racemic mixture of homochiral bis(pybox) complexes is formed.

Introduction

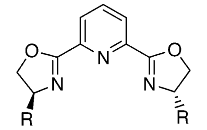
Enantiomerically pure cyanohydrins are valuable building blocks for pharmaceuticals and fine chemicals, and their synthesis has been the subject of several reviews and a recent (Nov 2004) *Tetrahedron Symposium in Print*.[1−4] The general method of synthesis involves addition of cyanide to a carbonyl compound (eq 1).



(1)

Three types of enantioselective catalysts are available for this reaction: enzymes, peptides, and chiral metal complexes. Enzymes and peptides can deliver impressive ee's but have disadvantages, including the requirement to use HCN as the cyanide source. In the past decade, attention has turned to chiral metal complexes, which will catalyze the addition of Me$_3$SiCN, and in this paper we report our results with lanthanide catalysis of this important reaction.

The hard Lewis acidity of the large Ln^{3+} ions (Ln = rare earth) results in highly labile Ln-to-ligand bonds in their complexes, which is an attractive feature in catalysis, though it can present serious difficulties in the development of enantioselective lanthanide-based catalysts.[5] Lanthanide compounds LnX$_3$ (X = chloride,[6] alkoxide,[7] CN,[8] OTf[9]) have been known for many years to be effective catalysts for the silylcyanation of aldehydes, giving high yields of racemic product. Shibasaki has reported an asymmetric cyanation−nitroaldol reaction catalyzed by Li$_3$[Y(binol)$_3$] using ethyl cyanoformate as the cyanide transfer reagent.[10] Our aim in the present work was to develop easy-to-use lanthanide-based catalysts for the enantioselective silylcyanation of aldehydes. We chose to investigate lanthanide complexes with the pybox ligand **1**,[11] which has several attractive features for our work: it is a strong donor with pyridine and imine N atoms, it is tridentate, binding as a rigid planar unit, and its steric properties can be tuned readily by an appropriate choice of substituents. A preliminary report of this work has already been published.[12] The reaction has also been investigated in a microreactor.[13]



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Since we began our work in this area, other groups have reported their results with enantioselective catalysis of aldehyde silylcyanation by lanthanide complexes derived from chiral ligands **1**,[14] **2**,[15] **3**,[16] **4**,[17] and **5** (Chart 1).[18] Chiral transition-metal complexes have

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(1) Effenberger, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1555−1564.

(2) Gregory, R. J. H. *Chem. Rev.* **1999**, *99*, 3649−3682.

(3) North, M. *Tetrahedron: Asymmetry* **2003**, *14*, 147−176.

(4) North, M. *Tetrahedron* **2004**, *60*, 10383−10384.

(5) Aspinall, H. C. *Chem. Rev.* **2002**, *102*, 1807.

(6) Vougioukas, A. E.; Kagan, H. B. *Tetrahedron Lett.* **1987**, *28*, 5513−5516.

(7) Ohno, H.; Mori, A.; Inoue, S. *Chem. Lett.* **1993**, 375−378.

(8) Utimoto, K.; Takai, T.; Kasuga, Y.; Matsubara, S. *Appl. Organomet. Chem.* **1995**, *9*, 413−419.

(9) Yang, Y.; Wang, D. *Synlett* **1997**, 1379−1380.

(10) Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3636−3638.

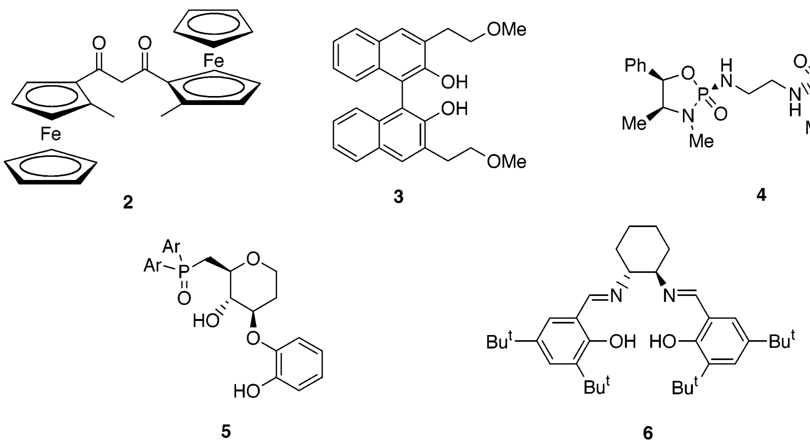
(11) Desimoni, G.; Faita, G.; Quadrelli, P. *Chem. Rev.* **2003**, *103*, 3119−3154.

(12) Aspinall, H. C.; Greeves, N.; Smith, P. M. *Tetrahedron Lett.* **1999**, *40*, 1763−1766.

(13) Jonsson, C. I.; Lundgren, S.; Haswell, S. J.; Moberg, C. *Tetrahedron* **2004**, *60*, 10515−10520.

10.1021/om050197+ CCC: $30.25

Chart 1



2 3 4 5 6

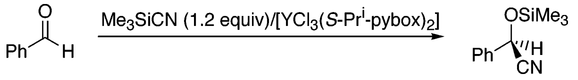
also been reported to catalyze the enantioselective formation of cyanohydrins; particular success has been achieved by Belokon and North using early-transition-metal complexes with the salen ligand **6**.[19]

Results and Discussion

The Catalytic Reaction. Although $Yb(OTf)_3$ has been reported to catalyze the addition of Me_3SiCN to carbonyl compounds[9] and to imines,[20] we found that complexes derived from $Ln(OTf)_3$ and pybox were inactive for the catalysis of aldehyde silylcyanation. We then turned our attention to anhydrous $LnCl_3$. Although anhydrous $LnCl_3$ is a little time-consuming to prepare and must be handled under rigorously anhydrous conditions, it has the advantage of a precisely known composition, whereas the hydrated $LnCl_3$ species contain quite variable amounts of water which may have a significant effect on catalytic behavior. Addition of 1 equiv of Pr^i-pybox to a THF slurry of anhydrous $PrCl_3$ resulted in partial dissolution of the $PrCl_3$, and the resulting solution catalyzed the addition of Me_3SiCN to benzaldehyde in high yield, albeit with a rather modest ee. The reaction was catalyzed only very slowly in the absence of Pr^i-pybox (5 days at room temperature was required for complete conversion), presumably due to the low solubility of $PrCl_3$ in THF. After this promising start, we investigated YCl_3 and were pleased to find that the smaller Y^{3+} ion gave rise to a substantial improvement in ee in the silylcyanation of benzaldehyde.

We then investigated a range of solvents, and our results are summarized in Table 1. The best ee's are obtained in polar solvents in which the catalyst shows good solubility, and MeCN was found to be the best. The potential of MeCN to act as a ligand for the Ln center does not appear to have an adverse effect on catalyst activity. In the case of protic solvents such as EtOH the unprotected cyanohydrin is formed directly by addition of HCN generated in situ by reaction of Me_3SiCN with the solvent. The poor performance of low-polarity solvents can be explained by the low solubility of the anhydrous catalyst in these media.

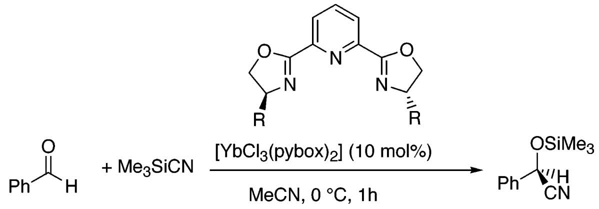
Table 1. Effect of Solvent on Enantioselective Silylcyanation of Benzaldehyde Catalyzed by $[YCl_3(Pr^i\text{-pybox})_2]^a$



solvent	reacn time^b/h	isolated yield/%	ee/%	comments
$PhCH_3$	3	97	26	not a homogeneous mixture
Et_2O	24	85	6	not a homogeneous mixture
$CHCl_3$	0.5	81	15	not a homogeneous mixture
CH_2Cl_2	3	91	49	not a homogeneous mixture
THF	3	91	49	
CH_3NO_2	3	85	49	
CH_3CN	1	88	67	
EtOH	24	69	54	

^{a} Conditions: 10 mol % catalyst, 25 °C, PhCHO:Me_3SiCN = 1:1.2. ^{b} Time for complete conversion of PhCHO as determined by TLC.

Table 2. Effect of Pybox Substituent on Enantioselective Silylcyanation of Benzaldehyde Catalyzed by $[YCl_3(pybox)_2]$



pybox substituent R	isolated yield/%	ee/%
Pr^i	87	67
Ph	77	80
CH_2Ph	>99	60
Bu^t	88	13

One of the attractive features of the pybox ligand is the possibility of steric tuning, and the effect of the pybox substituent on the $[YCl_3(pybox)_2]$-catalyzed silylcyanation of benzaldehyde is summarized in Table 2. In terms of enantioselectivity Ph-pybox is clearly the most effective ligand in the Y-catalyzed reaction, although the reactivity is somewhat reduced compared with that of the other ligands. Rather surprisingly, Bu^t-pybox gave very poor enantioselectivity, although the

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(14) Abiko, A.; Wang, G. Q. *Tetrahedron* **1998**, *54*, 11405−11420.

(15) Qian, C. T.; Zhu, C. J.; Huang, T. S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2131−2132.

(16) Yang, W. B.; Fang, J. M. *J. Org. Chem.* **1998**, *63*, 1356−1359.

(17) Yabu, K.; Masumoto, S.; Kanai, M.; Curran, D. P.; Shibasaki, M. *Tetrahedron Lett.* **2002**, *43*, 2923−2926.

(18) Masumoto, S.; Suzuki, M.; Kanai, M.; Shibasaki, M. *Tetrahedron Lett.* **2002**, *43*, 8647−8651.

(19) Belokon, Y. N.; Gutnov, A. V.; Moskalenko, M. A.; Yashkina, L. V.; Lesovoy, D. E.; Ikonnikov, N. S.; Larichev, V. S.; North, M. *Chem. Commun.* **2002**, 244−245.

(20) Kobayashi, S.; Ishitani, H.; Ueno, M. *Synlett* **1997**, 115.

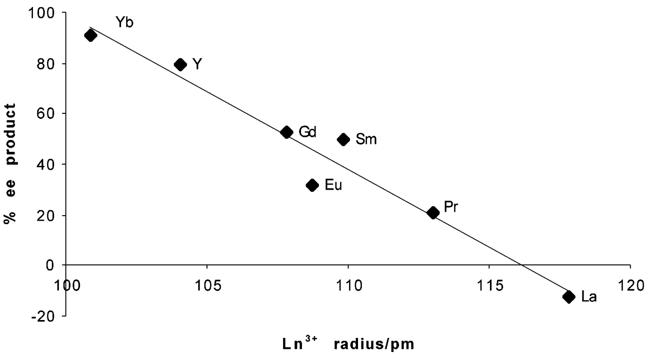


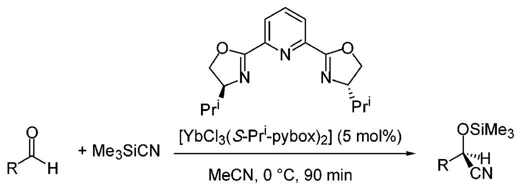
Figure 1. Variation of product ee with Ln^{3+} radius for the silylcyanation of benzaldehyde catalyzed by $[LnCl_3(Pr^i\text{-}pybox)_2]$.

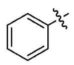
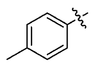
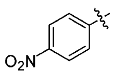
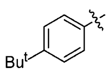
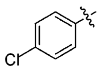
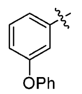
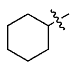
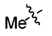
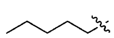
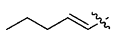
activity is still good, suggesting that access of the substrate to the catalytically active site is not a problem. Jacobsen found that Ph-pybox gave the best ee's in the $YbCl_3$-catalyzed ring opening of epoxides, with a reversal of enantioselectivity compared with Bu^t-pybox and Pr^i-pybox.[21] In our work we found that optimum enantioselectivity was achieved with a $LnCl_3$ to pybox ratio of 1:2, whereas the Jacobsen catalyst is proposed to be a Ln mono-pybox complex.

Effect of Ln^{3+} Radius on Reaction. The radius of Ln^{3+} ions decreases steadily from La^{3+} (six-coordinate radius 117.2 pm) to Lu^{3+} (six-coordinate radius 100.1 pm).[22] This decrease in radius leads to enhanced Lewis acidity for the smaller, later Ln^{3+} and also has a significant influence on the enantioselectivity of reactions, as the size of the chiral binding site is varied. Figure 1 shows a plot of product ee vs Ln^{3+} radius for the silylcyanation of benzaldehyde catalyzed by $[LnCl_3(Pr^i\text{-}pybox)_2]$.

The general increase in product ee with decreasing Ln^{3+} radius is not surprising; the smaller Ln^{3+} ions are expected to give a more tightly defined chiral binding site for the substrate and thus lead to increased enantioselectivity. Although Lu^{3+} is slightly smaller than Yb^{3+} (six-coordinate radius 100.1 pm; cf. 100.8 pm for Yb^{3+}), and may give slightly improved ee's, it is significantly more expensive than Yb and, thus, was not investigated in this work. The reversal of ee between Pr and La is a surprising feature of our work and is, as far as we know, unprecedented in lanthanide catalysis. A reversal of enantioselectivity between Sc^{3+} and La^{3+} has been observed in the $[Ln(OTf)_2(H_2O)_4(pybox)]^+$-catalyzed Diels−Alder reaction of 3-acryloyl-1,3-oxazolidin-2-one and cyclopentadiene;[23] however, given the very large difference in ionic radii (six-coordinate radius of Sc^{3+} 88.5 pm), it is possible that there are gross structural differences and, hence, different reactivity patterns between the La and Sc catalysts. Marks has observed a reversal of ee between Y and Lu in a catalytic intramolecular alkene hydroamination reaction, where the Y- and Lu-derived catalysts gave ee's of +43% and −29%, respectively.[24] Reversal of ee in lanthanide-catalyzed reactions has also been observed on changing temperature[25] and on addition of achiral ligands.[26] In our system catalysts prepared from Eu and Sm give ee's that show the greatest deviation from the generally linear trend. It is noteworthy that these two catalysts show markedly lower activities than those derived from other Ln species. For example, enantiomerically pure $[EuCl_3(Pr^i\text{-}pybox)_2]$ and $[SmCl_3(Pr^i\text{-}pybox)_2]$ give only ca. 30% and 74% yield of product, respectively, after 90 min at 0 °C. Under these conditions all of the other Ln species investigated gave essentially quantitative conversions.

Table 3. Enantioselective Silylcyanation of Aldehydes Catalyzed by $[YbCl_3(^iPr\text{-}pybox)_2]$



R	Hydrated $YbCl_3$ catalyst		Anhydrous $YbCl_3$ catalyst	
	Yield/%	ee/%	Yield/%	ee/%
	96	71	86	91
	22	64	89	80
	95	32	96	60
	56	0	88	88
			>99	80
			96	60
			86	60
			83	49
			61	45
			96	46
			88	58

Scope of the Catalytic Reaction. We investigated the scope of the reaction catalyzed by $[YbCl_3(Pr^i\text{-}pybox)_2]$. Although Ph-pybox gave rather better ee's than

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[21] Schaus, S. E.; Jacobsen, E. N. *Org. Lett.* **2000**, *2*, 1001−1004.

[22] Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

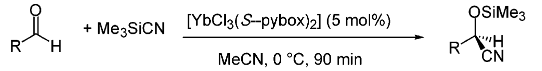
[23] Desimoni, G.; Faita, G.; Guala, M.; Laurenti, A. *Eur. J. Org. Chem.* **2004**, 3057−3062.

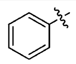
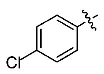
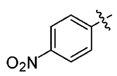
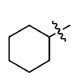
[24] Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagne, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241−10254.

[25] Giuseppone, N.; Santos, I.; Collin, J. *Tetrahedron Lett.* **2000**, *41*, 639−642.

[26] Kobayashi, S.; Ishitani, H. *J. Am. Chem. Soc.* **1994**, *116*, 4083−4084.

Table 4. Comparison of Ph-pybox and Pr^{i}-pybox for the Enantioselective Silylcyanation of Aldehydes Catalyzed by [YbCl$_3$(pybox)$_2$]



Substrate	Ph-pybox		Pr^{i}-pybox	
	Yield/%	Ee/%	Yield/%	Ee/%
	83	87	86	91
 Cl	31	52	99	80
 O$_2$N	37	14	96	60
	97	7	86	60

Pr^{i}-pybox in the [YCl$_3$(pybox)$_2$]-catalyzed reaction, we chose Pr^{i}-pybox because of the higher activity and the somewhat easier ligand synthesis. Results using 5 mol % of catalyst are summarized in Table 3. We also investigated the use of catalysts derived from hydrated LnCl$_3$, as these would be significantly easier to work with than their anhydrous counterparts. Jacobsen has reported the use of pybox complexes of hydrated LnCl$_3$ in the asymmetric ring opening of epoxides[21] and the hydrocyanation of hydrazones.[27] As seen in Table 3, results were poorer for the catalysts derived from hydrated YbCl$_3$, and we also found that conversions and ee's were much less reproducible.

We investigated a small number of substrates using the Ph-pybox ligand with YbCl$_3$, and the results are summarized in Table 4. Although results with benzaldehyde are similar to those obtained with the Pr^{i}-pybox catalyst, results with other substrates are very poor.

Studies with Varying ee's of Pybox. Investigations of the effect of ligand ee on product ee can give valuable mechanistic information about enantioselective catalytic reactions.[28] Jacobsen investigated the effect of pybox ee on product ee in the asymmetric ring opening of epoxides catalyzed by lanthanide chloride pybox complexes and found a marked positive nonlinear effect which was ascribed to a reaction involving two molecules of catalyst: one acting as a Lewis acid and the other as a cyanide transfer agent.[21]

We investigated the effect of ee of pybox on the outcome of the silylcyanation of benzaldehyde for several Ln species. The results for Yb and Gd catalysts, which both show essentially quantitative conversion with catalysts prepared from ligand of any ee, are shown in Figure 2. There is a clear linear dependence of product ee on pybox ee, ruling out the possibility of a bimetallic transition state of the type proposed by Jacobsen.

The behavior of the [EuCl$_3$(Pr^{i}-pybox)$_2$] catalyst is very different from that of the Yb and Gd analogues, as

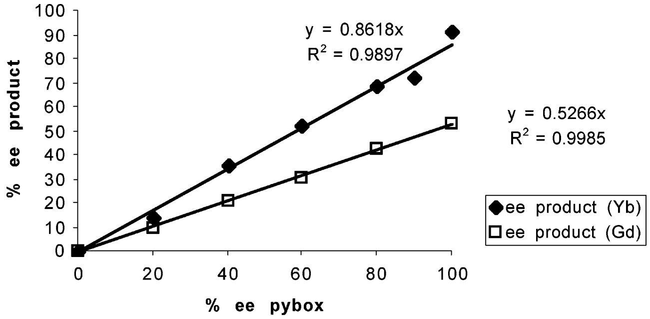


Figure 2. Dependence of product ee on the ee of the pybox ligand in the silylcyanation of benzaldehyde.

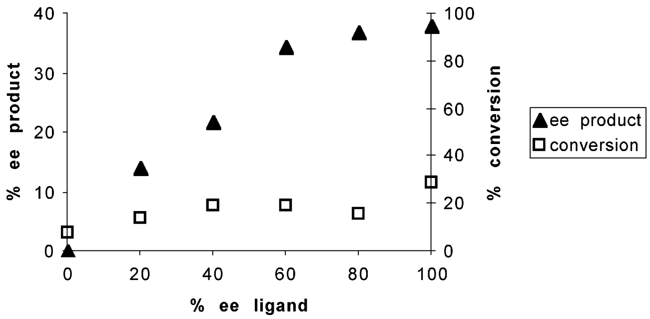


Figure 3. Dependence of product ee on the ee of the pybox ligand in the silylcyanation of benzaldehyde catalyzed by [EuCl$_3$(Pr^{i}-pybox)$_2$].

shown in Figure 3. There is a clear deviation from linearity in the dependence of product ee on ligand ee, and conversions are very poor (a maximum of <30% for catalyst prepared from enantiomerically pure ligand and less than 5% for racemic ligand) compared with essentially quantitative conversions for Yb and Gd. [SmCl$_3$(Pr^{i}-pybox)$_2$] also showed rather poor conversions, especially when prepared from enantiomerically impure pybox. Conversions and product ee's were both found to be highly sensitive to catalyst concentration in the Sm-catalyzed reaction, and the catalyst showed rather poor solubility.

We did not investigate the effect of pybox ee on product ee for the La-catalyzed reaction, as absolute values of ee would be too small to be meaningful.

The linearity of the dependence of product ee on pybox ee for Yb and Gd indicates that there is not a bimetallic intermediate in the catalyst, as proposed for the YbCl$_3$/pybox-catalyzed asymmetric ring opening of epoxides.[21] Our observations are consistent with a significant change in behavior around Eu, where conversions and ee's are both found to be very dependent on pybox ee.

Characterization of Ln Pybox Complexes. (a) Pybox Complexes of Lanthanide Chlorides. Pybox complexes of LnCl$_3$ were clearly the most relevant to our catalytic studies and therefore of the greatest interest to us. We found early in our investigations that addition of 1 equiv of pybox to a slurry of LnCl$_3$ in THF resulted in dissolution of only part of the LnCl$_3$. A powdery solid was precipitated from the supernatant solution by careful addition of Et$_2$O, and FAB mass spectrometry and elemental analysis showed this to be [LnCl$_3$(pybox)$_2$]. Catalytic reactions performed using this material showed reactivity similar to those using catalysts prepared in situ using the optimum pybox:LnCl$_3$ ratio of 2:1. Jacobsen has reported that pybox:

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(27) Keith, J. M.; Jacobsen, E. N. *Org. Lett.* **2004**, *6*, 153–155.
(28) Kagan, H. B. *Synlett* **2001**, 888–899.

$LnCl_3$ ratios ranging from 1.2:1 to 2:1 gave similar results in the enantioselective hydrocyanation of hydrazones, but the higher pybox:$LnCl_3$ ratios gave more soluble catalysts; however, as hydrated $LnCl_3$ species were used, these results may not be directly relevant to our observations.[27] [$LnCl_3$(pybox)$_2$] defied all our attempts to grow X-ray-quality crystals from THF and either Et_2O or petroleum ether. However, we were able to grow good-quality crystals by addition of Et_2O to a concentrated MeCN solution of [$LnCl_3$(Pr^i-pybox)$_2$] (Ln = Eu, Yb) at −18 °C.

X-ray diffraction showed these crystals to be the salt [$LnCl_2$(Pr^i-pybox)$_2$][$LnCl_4$(Pr^i-pybox)], where halide transfer has occurred in a Lewis acid−Lewis base reaction, and one Pr^i-pybox ligand has dissociated due to steric congestion. This halide transfer reaction is well documented in the chemistry of $LnCl_3$: [$LnCl_2$(THF)$_5$][$LnCl_4$(THF)$_2$] species have been characterized for Ln = Gd, Er,[29] Dy,[30] Tb.[31] [$LnCl_2$(Pr^i-pybox)$_2$][$LnCl_4$(Pr^i-pybox)] salts do not show good catalytic activity, and therefore, they are not catalyst precursors in the silylcyanation reaction. However, the structures are of interest as the only examples of characterized [$LnCl_3$(pybox)] complexes.

Parts a and b of Figure 4 show ORTEP plots of the cation and anion of [$YbCl_2$(Pr^i-pybox)$_2$][$YbCl_4$(Pr^i-pybox)], respectively. [$EuCl_2$(Pr^i-pybox)$_2$][$EuCl_4$(Pr^i-pybox)] has a very similar structure (although it crystallizes with two molecules of MeCN in the lattice, whereas the Yb salt crystallizes with three molecules of MeCN), and the cation and anion are shown in parts a and b of Figure 5, respectively. The eight-coordinate [$YbCl_2$(Pr^i-pybox)$_2$]$^+$ ion shows a somewhat distorted dodecahedral geometry with Yb−Cl distances in the range observed for analogous [$YbCl_2L_n$]$^+$ complexes. The geometry of the seven-coordinate [$YbCl_4$(Pr^i-pybox)]$^-$ ion is approximately pentagonal bipyramidal, with Cl ligands occupying both axial sites and two of the equatorial sites. Again Yb−Cl distances are within the range observed for other [$YbCl_4L_n$]$^-$ complexes. The interplanar angle for the two pybox ligands of [$YbCl_2$(Pr^i-pybox)$_2$]$^+$ (defined by Yb1, N1, N2 and Yb1, N5, N6) is 82.6°. The corresponding angle for [$EuCl_2$(Pr^i-pybox)$_2$]$^+$ (defined by Eu1, N1, N2 and Eu1, N4, N5) is 93.2°. The larger angle between the pybox ligands in the Eu complex may be due to the larger radius of Eu^{3+} compared with that of Yb^{3+}, leading to reduction in steric crowding in the Eu complex.

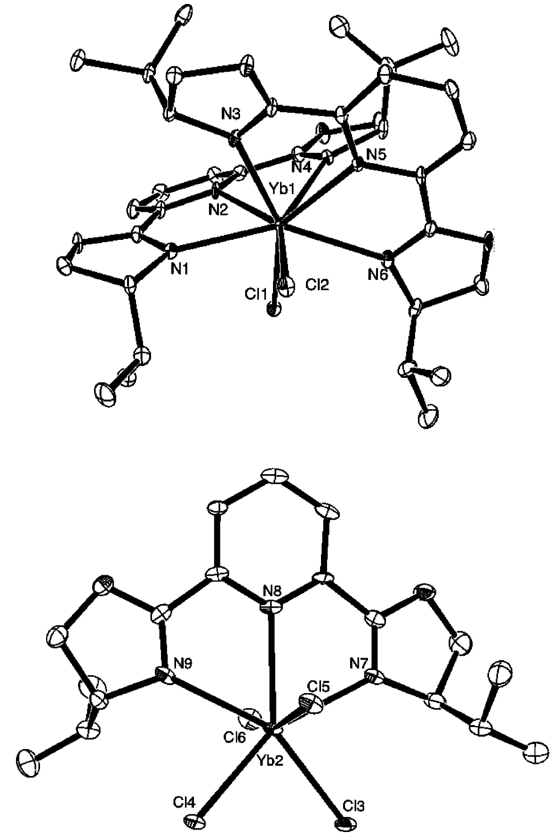

Figure 4. (a, top) ORTEP plot (30% probability) of [$YbCl_2$(S-Pr^i-pybox)$_2$]$^+$. Selected distances (Å) and angles (deg): Yb1−N1, 2.490(7); Yb1−N2, 2.508(8); Yb1−N4, 2.545(8); Yb1−N3, 2.483(8); Yb1−N5, 2.482(7); Yb1−N6, 2.513; Yb1−Cl1, 2.570(2); Yb1−Cl2, 2.562(2); N1−Yb1−N2, 65.1(3); N2−Yb1−N4, 64.5(3); N3−Yb1−N5, 65.3(2); Cl1−Yb1−Cl2, 101.69(8); Cl1−Yb1−N2, 73.75(19); Cl2−Yb1−N5, 77.12(19). (b, bottom) ORTEP plot (30% probability) of [$YbCl_4$(S-Pr^i-pybox)]$^-$. Selected distances (Å) and angles (deg): Yb2−N7, 2.508(9); Yb2−N8, 2.581(8); Yb2−N9, 2.523(9); Yb2−Cl3, 2.596(3); Yb2−Cl4, 2.625(2); Yb2−Cl5, 2.545(2); Yb2−Cl6, 2.574(2); N8−Yb2−N9, 63.0(3); N8−Yb2−N7, 63.7(3); Cl3−Yb2−Cl4, 81.95(9); Cl5−Yb2−Cl6, 162.83(9); Cl5−Yb2−N8, 81.71(17); Cl6−Yb2−N8, 82.02(18).

(b) Pybox Complexes of Lanthanide Triflates. Although we found that pybox complexes of Ln(OTf)$_3$ were inactive for catalysis of aldehyde silylcyanation, there are reports of enantioselective catalysis by crystallographically characterized mono-pybox complexes of rare-earth triflates. For example, [Sc(OTf)$_3$(H_2O)(Ph-pybox)] catalyzes the enantioselective synthesis of homopropargylic alcohols[32] and [La(OTf)$_2$(H_2O)$_4$(pybox)]$^+$ catalyzes the enantioselective Mukaiyama−Michael[33] and Diels−Alder[23] reactions. It is not surprising that coordination of pybox to the small Sc^{3+} ion forms an effective chiral binding site. The effectiveness of a single pybox ligand in a La(OTf)$_2$ catalyst is perhaps more surprising, but this catalyst contains four coordinated H_2O ligands which contribute significantly to the filling of the La coordination sphere, and the substrate in the reaction chelates to the catalyst.

Because of the difficulties in crystallizing [$LnCl_3$(pybox)$_2$] complexes, we investigated the coordination chemistry of Ln(OTf)$_3$ with pybox. The increased solubility of Ln(OTf)$_3$ compared with that of anhydrous $LnCl_3$ makes these compounds much easier to work with. The hard Lewis acidity of Ln^{3+} ions means that their coordination chemistry is governed almost entirely by steric factors; therefore, the binding of the pybox ligand is not significantly affected by the identity of the anion. We always used carefully dried Ln(OTf)$_3$ for the preparation of [Ln(OTf)$_3$(pybox)] complexes and found that the bis-pybox complexes [Ln(OTf)$_3$(pybox)$_2$] were

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(29) Deacon, G. B.; Feng, T.; Junk, P. C.; Skelton, B. W.; Sobolev, A. N.; White, A. H. *Aust. J. Chem.* **1998**, *51*, 75−89.

(30) Willey, G. R.; Meehan, P. R.; Woodman, T. J.; Drew, M. G. B. *Polyhedron* **1997**, *16*, 623−627.

(31) Evans, W. J.; Shreeve, J. L.; Ziller, J. W.; Doedens, R. J. *Inorg. Chem.* **1995**, *34*, 576−585.

(32) Evans, D. A.; Sweeney, Z. K.; Rovis, T.; Tedrow, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 12095−12096.

(33) Desimoni, G.; Faita, G.; Filippone, S.; Mella, M.; Zampori, M. G.; Zema, M. *Tetrahedron* **2001**, *57*, 10203−10212.

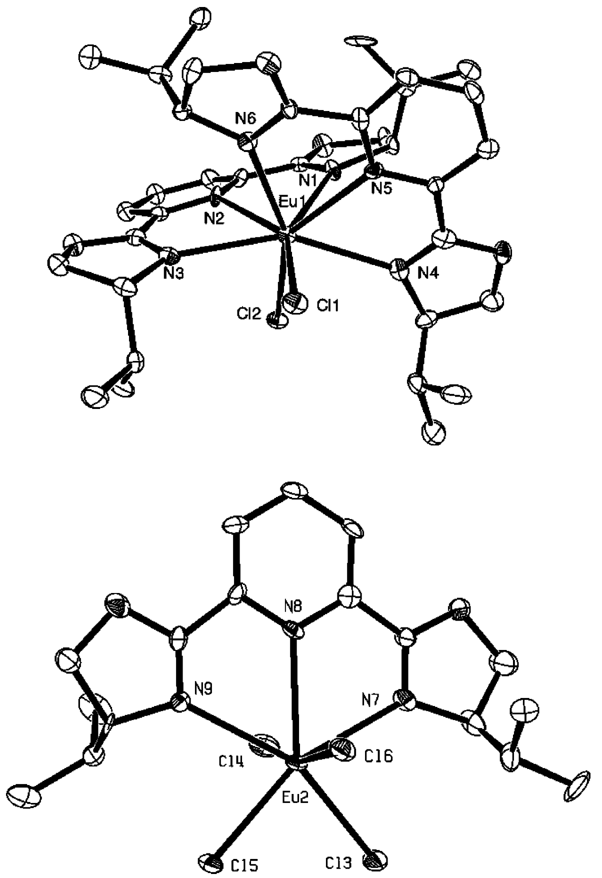

Figure 5. (a, top) ORTEP plot (30% probability) of $[EuCl_2(S\text{-}Pr^i\text{-pybox})_2]^+$. Selected distances (Å) and angles (deg): Eu1–N1, 2.604(12); Eu1–N2, 2.595(11); Eu1–N3, 2.572(10); Eu1–N4, 2.567(10); Eu1–N5, 2.600(12); Eu1–N6, 2.539(12); Eu1–Cl1, 2.633(4); Eu1–Cl2, 2.633(4); N1–Eu1–N2, 62.7(4); N2–Eu1–N3, 63.0(4); N4–Eu1–N5, 62.5(4); N5–Eu1–N6, 63.4(4); Cl1–Eu1–Cl2, 101.49; Cl1–Eu1–N5, 78.7(3); Cl2–Eu1–N2, 73.5(3). (b, bottom) ORTEP plot (30% probability) of $[EuCl_4(S\text{-}Pr^i\text{-pybox})]^-$. Selected distances (Å) and angles (deg): Eu2–N7, 2.594(12); Eu2–N8, 2.658(12); Eu2–N9, 2.625(12); Eu2–Cl3, 2.655(4); Eu2–Cl4, 2.657(4); Eu2–Cl5, 2.685(4); Eu2–Cl6, 2.628(4); N7–Eu2–N8, 62.1(4); N8–Eu2–N9, 61.4(4); Cl3–Eu2–Cl5, 89.35(14); Cl4–Eu2–Cl6, 166.31(13); Cl6–Eu2–N8, 85.4(3); Cl4–Eu2–N8, 81.5(3).

formed selectively. We believe that these complexes, although themselves not active as catalysts or precatalysts for the enantioselective silylcyanation of aldehydes, give some useful information about the structures of $Ln(pybox)_2$ complexes.

$[La(OTf)_3(S\text{-}Pr^i\text{-pybox})_2]$ crystallized from THF/petroleum ether, and its structure is shown in Figure 6. The complex is nine-coordinate, and the angle between the planes of the two pybox ligands (defined by the planes La1, N4, N5 and La1, N1, N2) is 64.7°. This is a much smaller interplanar angle than those observed for $[EuCl_2(Pr^i\text{-pybox})_2]^+$ (93.2°) and $[YbCl_2(Pr^i\text{-pybox})_2]^+$ (82.6°) and is probably a consequence of the higher coordination number for the La complex (9 vs 8).

Figure 7 shows Ln(pybox) fragments for $[Sc(OTf)_3(H_2O)(Ph\text{-pybox})]$,[32] $[La(OTf)_2(H_2O)_4(pybox)]^+$,[33] and $[La(OTf)_3(Pr^i\text{-pybox})_2]$. From these pictures it is clear that the Pr^i-pybox ligand does not have sufficient steric reach to define an effective chiral binding site for a monodentate substrate at a large Ln^{3+} center.

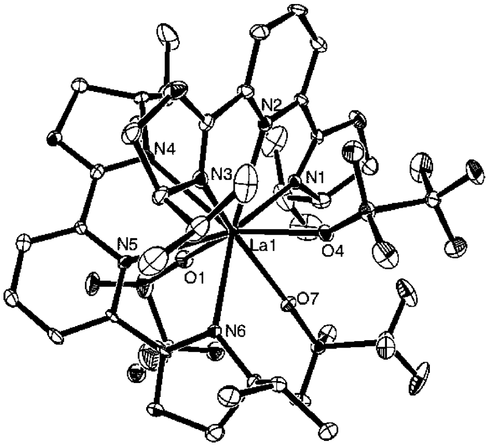

Figure 6. ORTEP plot (30% probability) of $[La(OTf)_3(S\text{-}Pr^i\text{-pybox})_2]$. Selected distances (Å) and angles (deg): La1–N1, 2.662(5); La1–N2, 2.698(5); La1–N3, 2.716(5); La1–N4, 2.754(5); La1–N5, 2.704(5); La1–N6, 2.688(4); La1–O1, 2.491(4); La1–O4, 2.509(4); La1–O7, 2.511(4); N1–La1–N2, 61.33(15); N2–La1–N3, 61.11(15); N4–La1–N5, 60.61(14); N5–La1–N6, 60.72(14).

There are a small number of examples of structurally characterized bis-pybox complexes in the Cambridge Crystallographic Database.[34] These are all six-coordinate transition-metal complexes with close to octahedral geometry and are therefore not comparable to the lanthanide complexes we report here. The coordinative saturation of the transition-metal bis-pybox complexes results in them all being catalytically inactive. The much larger Ln^{3+} ions can accommodate higher coordination numbers, and thus, the bis-pybox complexes are sufficiently coordinatively unsaturated to be catalytically active.

(c) Diastereoselectivity in the Formation of Bis-pybox Complexes. Selective formation of heterochiral $[M(pybox)_2]^{2+}$ complexes has been observed with Ph-pybox and transition metals. In the case of complexes of Cu^{2+} and Zn^{2+} these observations were made as part of an investigation into nonlinear effects in enantioselective catalysis, and the complexes were crystallographically characterized. Evans[35] and Jørgensen[36] had both observed significant positive nonlinear effects in reactions catalyzed by $[M(Ph\text{-pybox})]^{2+}$ (M = Cu, Zn), and both groups observed that, even using a M:pybox ratio of 1:1, racemic Ph-pybox gave exclusively the poorly soluble complex $[M(R\text{-Ph-pybox})(S\text{-Ph-pybox})]^{2+}$, which was catalytically inactive. Investigations of Co^{2+} coordination chemistry by Williams[37] showed that heterochiral $[Co(pybox)_2]$ was formed selectively when R = Ph, but mixtures of homo- and heterochiral complexes were formed with R = Me, Bz. This diastereoselectivity was explained by the avoidance of steric interference between Ph substituents on different ligands in the heterochiral complex and the possibility of favorable π-stacking interactions between the Ph substituents of

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(34) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746–749.

(35) Evans, D. A.; Kozlowski, M. C.; Murry, J. A.; Burgey, C. S.; Campos, K. R.; Connell, B. T.; Staples, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 669–685.

(36) Saaby, S.; Nakama, K.; Lie, M. A.; Hazell, R. G.; Jorgensen, K. A. *Chem. Eur. J.* **2003**, *9*, 6145–6154.

(37) Provent, C.; Bernardinelli, G.; Williams, A. F.; Vulliermet, N. *Eur. J. Inorg. Chem.* **2001**, 1963–1967.

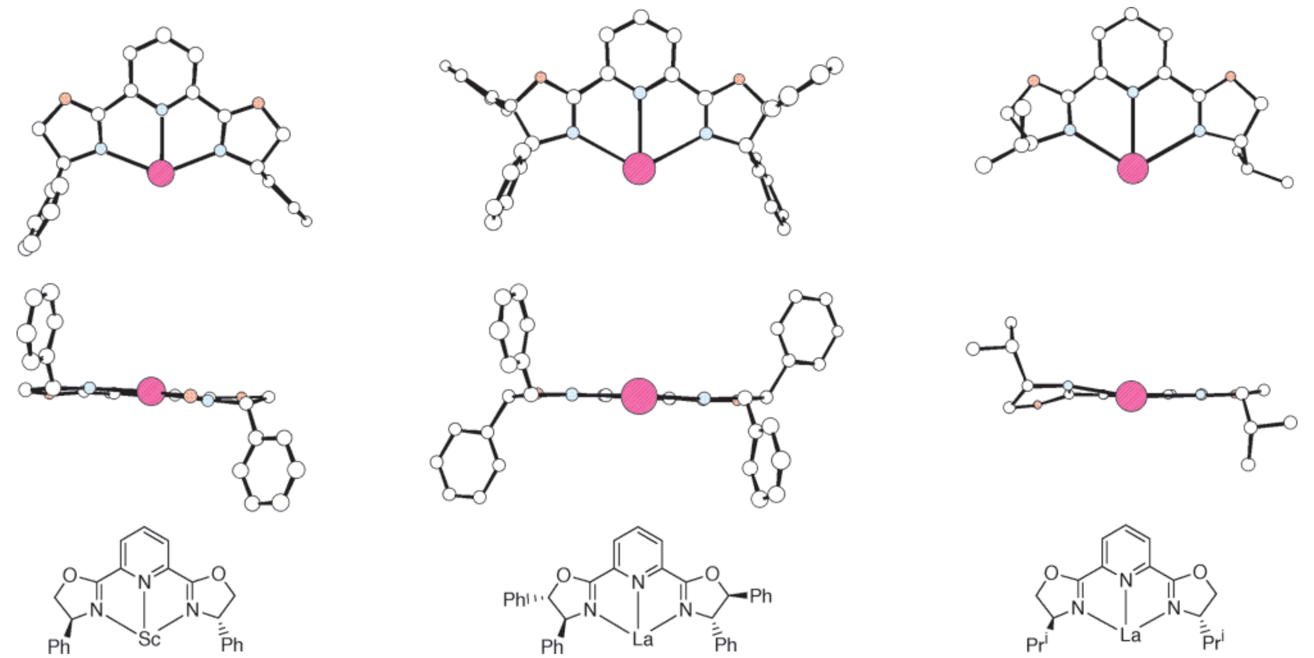

Figure 7. Structures of rare-earth pybox complexes.

one pybox ligand with the pyridine ring of the other pybox ligand.

When $[LnX_3(pybox)_2]$ is prepared by reaction of LnX_3 with racemic pybox, there are three possible outcomes: (i) exclusive formation of the heterochiral complex $[LnX_3(R\text{-pybox})(S\text{-pybox})]$; (ii) exclusive formation of a racemic mixture of homochiral complexes $[LnX_3(R\text{-pybox})_2]$ and $[LnX_3(S\text{-pybox})_2]$; (iii) formation of a mixture of homo- and heterochiral complexes. We have previously found that diastereoselectivity in the reactions of $[Ln\{N(SiMe_3)_2\}_3]$ with racemic LiHbinol (H_2binol = binaphthol) to give $Li_3[Ln(binol)_3]$ is dependent on Ln^{3+} radius.[38] We found that the outcome of the reaction of $Ln(OTf)_3$ with 2 equiv of racemic Pr^i-pybox is also dependent on the Ln^{3+} radius: $Eu(OTf)_3$ gives *exclusively* the heterochiral complex $[Eu(OTf)_3(R\text{-pybox})(S\text{-pybox})]$, and $Yb(OTf)_3$ gives *exclusively* a racemic mixture of homochiral complexes $[Yb(OTf)_2(R\text{-pybox})_2]^+$ and $[Yb(OTf)_2(S\text{-pybox})_2]^+$. Due to disorder in the triflate ligands, we were unable to refine the crystal structures fully; however, the essential structural details have been established and the structures of $[Yb(OTf)_2(S\text{-}Pr^i\text{-pybox})_2]^+$ and $[Eu(OTf)_2(H_2O)(R\text{-}Pr^i\text{-pybox})(S\text{-}Pr^i\text{-pybox})]^+$ are shown in Figures 8 and 9, respectively. $[Yb(OTf)_2(Pr^i\text{-pybox})_2][OTf]$ crystallizes with four symmetry-related molecules in the unit cell: two molecules of $[Yb(OTf)_2(R\text{-pybox})_2]^+$ and two molecules of $[Yb(OTf)(S\text{-pybox})_2]^+$. There are no obvious steric interactions that would account for this difference in behavior, and diastereoselectivity in the formation of Pr^i-pybox complexes has not previously been reported. The angle between the pybox planes of $[Yb(OTf)_2(S\text{-}Pr^i\text{-pybox})_2]^+$ is 95.1°, significantly larger than the corresponding angle (82.6°) for $[YbCl_2(R\text{-}Pr^i\text{-pybox})_2]^+$. Steric congestion at the smaller Yb^{3+} center compared with La^{3+} has resulted in the ejection of one OTf^- from the coordination sphere. Analysis of bond angles at Yb indicate that the coordination geometry is approximately bicapped trigonal prismatic.[39] $[Eu(OTf)_2(H_2O)(R\text{-}Pr^i\text{-pybox})(S\text{-}Pr^i\text{-pybox})][OTf]$ crystallizes with two independent molecules in the unit cell (see Figure 9); the two complexes differ in the relative dispositions of the two pybox ligands, illustrating the very flexible coordination geometry that is observed at lanthanide centers. The interplanar angle between the pybox ligands is 73.1° for molecule 1 and 95.5° for molecule 2.

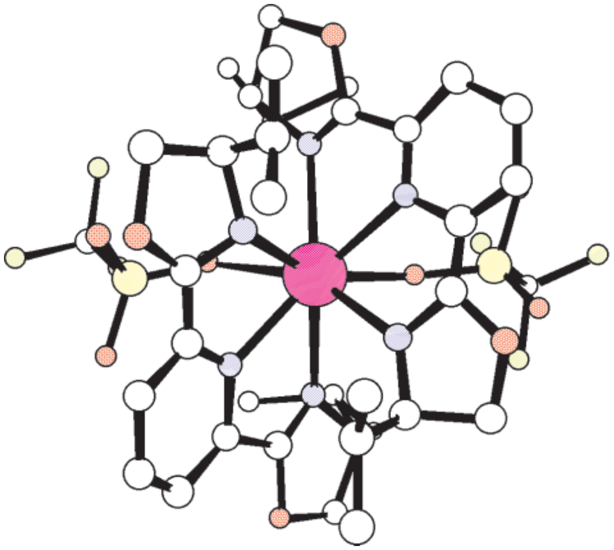

Figure 8. Structure of $[Yb(OTf)_2(S\text{-}Pr^i\text{-pybox})_2]^+$.

Mechanism of the Catalytic Reaction. From the combination of our structural and reactivity studies we are able to make some general comments on the mechanism of the silylcyanation of aldehydes catalyzed by $[LnCl_3(pybox)_2]$ complexes. $[LnCl_3(Pr^i\text{-pybox})_2]$ species are partially dissociated in MeCN solution, as shown by conductivity measurements (10^{-3} M solution, Ln = Yb, 18.5 °C, 63 μS; Ln = Eu, 20 °C, 172 μS). ^1H NMR spectroscopy does not show any uncoordinated pybox, proving that this dissociation is not forming

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(38) Aspinall, H. C.; Bickley, J. F.; Dwyer, J. L. M.; Greeves, N.; Kelly, R. V.; Steiner, A. *Organometallics* **2000**, *19*, 5416−5423.

(39) Haigh, C. W. *Polyhedron* **1995**, *14*, 2871−2878.

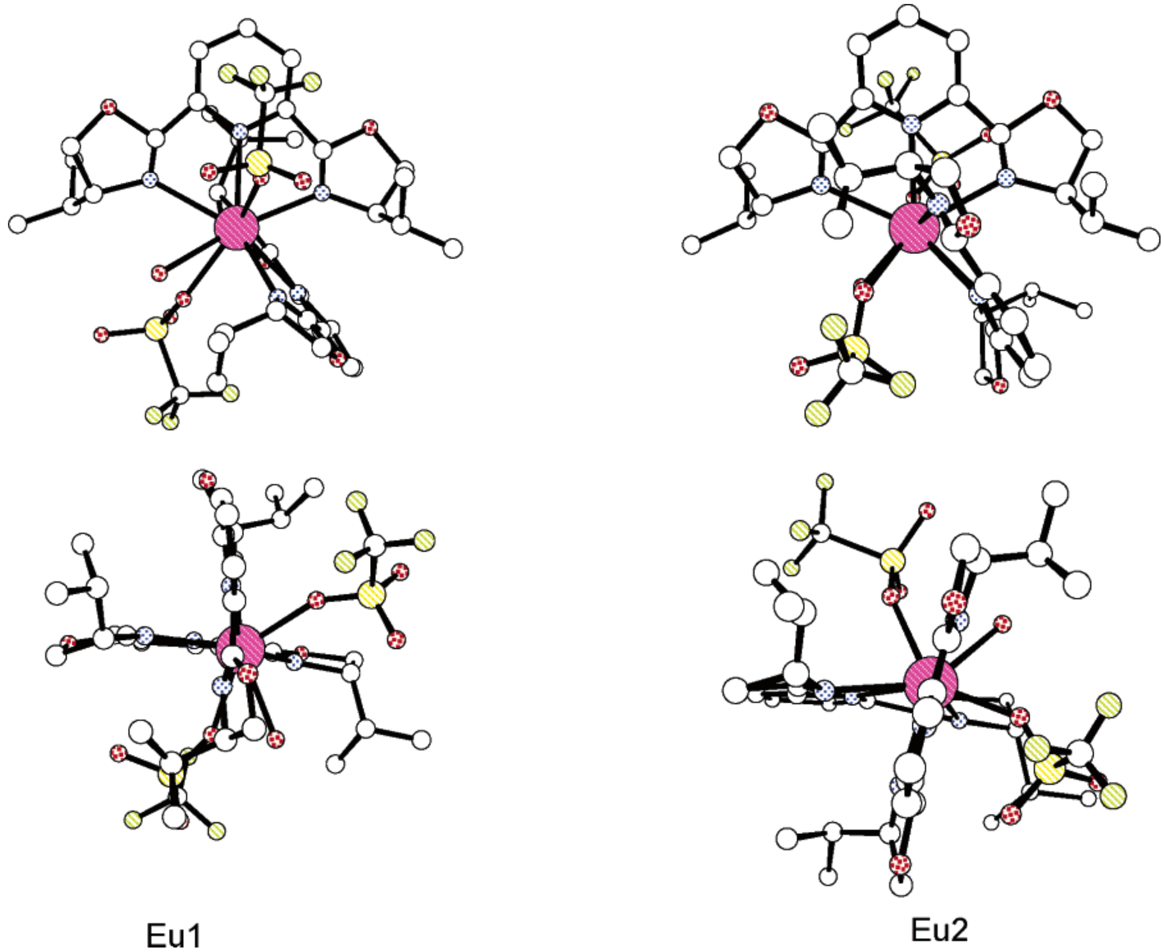
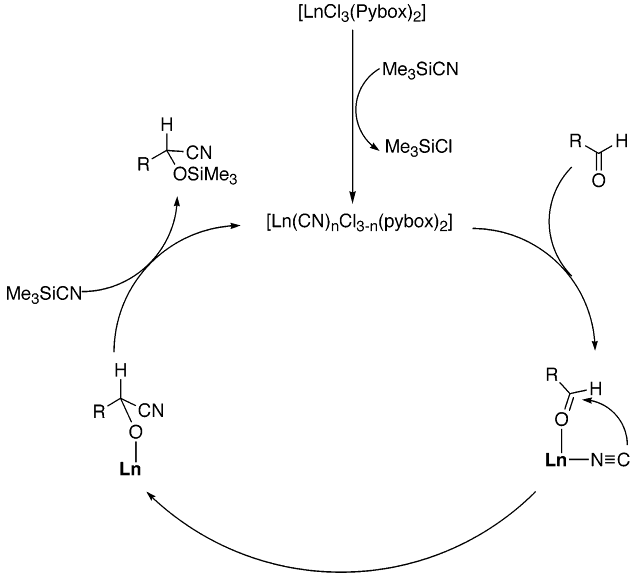


Figure 9. Structures of the two crystallographically independent molecules of $[Eu(OTf)_2(H_2O)(R\text{-}Pr^i\text{-pybox})(S\text{-}Pr^i\text{-pybox})]^+$.

significant quantities of the salt $[LnCl_2(Pr^i\text{-pybox})_2][LnCl_4(Pr^i\text{-pybox})]$, which was characterized by X-ray diffraction. Addition of 1 equiv of NaX (X = BPh_4, BF_4) to a MeCN solution of $[LnCl_3(Pr^i\text{-pybox})_2]$ results in precipitation of NaCl, and $[LnCl_2(Pr^i\text{-pybox})_2][X]$ can be isolated from the supernatant solution. These salts are much less effective in catalysis than the parent $[YbCl_3(Pr^i\text{-pybox})_2]$: in the silylcyanation of benzaldehyde $[YbCl_2(Pr^i\text{-pybox})_2][BF_4]$ gave a conversion of 85% and an ee of 57%, and the corresponding BPh_4^- salt gave only 12% conversion and 12% ee. This indicates that the cationic $[LnCl_2(Pr^i\text{-pybox})_2]^+$ is not the active catalytic species.

The paramagnetic nature of $Yb^{3+}(4f^{13})$ gives rise to significant shifting of ligand proton resonances in the ^1H NMR spectrum; however, the NMR spectrum of a CD_3CN solution of PhCHO and $[YbCl_3(Pr^i\text{-pybox})_2]$ in a molar ratio of 1:1 shows no shifting of aldehyde proton. This indicates that $[YbCl_3(Pr^i\text{-pybox})_2]$ is not significantly Lewis acidic and thus is a catalyst precursor rather than the active catalyst. We have found by ^1H NMR spectroscopy that addition of Me_3SiCN to a CD_3CN solution of $[YbCl_3(Pr^i\text{-pybox})_2]$ results in formation of Me_3SiCl and, presumably, $[Yb(CN)_nCl_{3-n}(Pr^i\text{-pybox})_2]$, which we propose to be the catalytically active species. Jacobsen has made a similar suggestion for the $[YbCl_3(H_2O)_n(pybox)]$-catalyzed asymmetric ring opening of epoxides by Me_3SiCN.[21] The absence of any nonlinear effects in the $[LnCl_3(Pr^i\text{-pybox})_2]$ (Ln = Yb, Gd) catalyzed reaction is consistent with our observation that homochiral $Yb(pybox)_2$ complexes are formed on reaction of $Yb(OTf)_3$ with racemic pybox and also indicate a monometallic intermediate in the catalytic reaction. We therefore propose that the reaction proceeds via an intramolecular cyanide transfer. as outlined in Scheme 1.

Scheme 1. Proposed Cycle for the Silylcyanation of Aldehydes Catalyzed by $[LnCl_3(pybox)_2]$



Little is known about monomeric complexes of lanthanide cyanides: the Cambridge Crystallographic

Database contains no examples of such compounds, and so there is no evidence of how the ambidentate CN^- ligand would bind to a hard Ln center. CN^- binds to Ln through both C and N when it acts as a bridging ligand in the cyclic trimer $[(C_5Me_5)_2Sm(\mu_2\text{-}CN)(Bu^tCN)]_3$.[40] There are many examples of CN^- bridging between a transition metal and Ln,[41] and in these cases CN^- is invariably bonded to Ln through the N atom. It is therefore likely that the CN^- is N-bonded to Ln in our catalytic system. Corey has recently proposed an isocyanide species derived from reaction of Ph_3PO with Me_3SiCN as the cyanide transfer agent in the catalytic silylcyanation of aldehydes.[42]

Conclusions

$[LnCl_3(pybox)_2]$ catalyzes the enantioselective silylcyanation of a range of aromatic and aliphatic aldehydes with excellent conversions and ee's of up to 91% under mild conditions. The catalyst must be prepared from anhydrous $LnCl_3$: use of hydrated $LnCl_3$ results in poorer and much less reproducible results. The outcome of the reaction (ee and conversion) are both dependent on the pybox substituent and the radius of Ln^{3+}; the best ee's and conversions are obtained with Pr^i-pybox and Ln = Yb. Studies with catalysts derived from pybox of varying enantiomeric purity show no nonlinear effects for Ln = Yb, Gd, consistent with a monometallic reaction intermediate. A catalytic cycle involving intramolecular CN transfer to a coordinated aldehyde is proposed. Diastereoselectivity in the formation of $[Ln(OTf)_3(Pr^i\text{-pybox})_2]$ is found to depend on the ionic radius of Ln^{3+}: reaction of 2 equiv of racemic Pr^i-pybox with $[Eu(OTf)_3]$ gives exclusively the heterochiral complex $[Eu(OTf)_3(R\text{-}Pr^i\text{-pybox})(S\text{-}Pr^i\text{-pybox})]$, whereas with $[Yb(OTf)_3]$ a racemic mixture of the homochiral complexes $[Yb(OTf)_2(R\text{-}Pr^i\text{-pybox})_2]^+$ and $[Yb(OTf)_2(S\text{-}Pr^i\text{-pybox})_2]^+$ is formed.

Experimental Section

The preparation of all lanthanide complexes was performed under strictly anaerobic and anhydrous conditions using standard Schlenk techniques. Nondeuterated solvents were distilled from sodium/benzophenone ketyl and stored under N_2 over activated 4 Å molecular sieves prior to use. Deuterated solvents were distilled from CaH_2 prior to use.

Anhydrous lanthanide chlorides were prepared by heating $LnCl_3{\cdot}nH_2O$ in vacuo in the presence of NH_4Cl.[43] Lanthanide triflates were prepared by reactions of Ln_2O_3 with HOTf in H_2O. pybox ligands were prepared by a slight modification of the literature procedure.[44]

NMR spectra were recorded on a Bruker Avance 400 spectrometer. NMR samples of lanthanide complexes were sealed under vacuum. Mass spectra of lanthanide complexes were recorded on a VG Analytical 7070E double-focusing spectrometer with an FAB gun running at 8 kV and 1 mA emission. Xe was used as the FAB gas and *m*-nitrobenzyl alcohol as the matrix compound. Elemental analyses were performed in duplicate by Mr. S. Apter of this department, using a Carlo Erba 1106 analyzer.

Preparation of $[YbCl_3(S\text{-}Pr^i\text{-pybox})_2]$. A solution of S-Pr^i-pybox (0.650 g, 2.16 mmol) in MeCN (50 cm^3 was added to anhydrous $YbCl_3$ (0.307 g, 1.08 mmol) in a Schlenk flask. The reaction mixture was stirred at room temperature to give a clear, colorless solution. The solution was concentrated, and the product was precipitated out as a microcrystalline solid by addition of Et_2O.

FAB mass spectrum: $[M - Cl]^+$ *m/z* 846.4 ($[YbCl_2(Pr^i\text{-pybox})_2]$ = 846.2); $[M - Cl - Pr^i - pybox]^+$ *m/z* 545.1 ($[YbCl_2(pybox)]$ = 545.1).

Other $[LnCl_3(Pr^i\text{-pybox})_2]$ complexes were prepared in a similar way.

$[EuCl_3(S\text{-}Pr^i\text{-pybox})_2]$. FAB mass spectrum: $[M - Cl]^+$ *m/z* 825.2 ($[EuCl_2(Pr^i\text{-pybox})_2]$ = 825.2); $[M - Cl - (Pr^i\text{-pybox})]^+$ *m/z* 523.9 ($[YbCl_2(pybox)]$ = 524.0).

***rac*-$[YbCl_3(Pr^i\text{-pybox})_2]$.** FAB mass spectrum: $[M - Cl]^+$ *m/z* 846.4; $[M - Cl - (Pr^i\text{-pybox})]^+$ *m/z* 545.1.

***rac*-$[EuCl_3(Pr^i\text{-pybox})_2]$.** FAB mass spectrum: $[M - Cl]^+$ *m/z* 825.2; $[M - Cl - (Pr^i\text{-pybox})]^+$ *m/z* 523.9.

Preparation of $[Yb(OTf)_3(Pr^i\text{-pybox})_2]$. $Yb(OTf)_3{\cdot}nH_2O$ (0.759 mmol) was dried in vacuo (5 h, 150 °C). A solution of S-Pr^i-pybox (0.460 g, 1.53 mmol) in THF (50 cm^3) was added, and the reaction mixture was stirred at room temperature to give a clear, colorless solution. The solution was concentrated in vacuo, and the product was precipitated out as a microcrystalline solid by careful addition of Et_2O.

FAB mass spectrum: $[M - OTf]^+$ *m/z* 1074.4 ($[Yb(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 1074.2); $[M - OTf - Pr^i\text{-pybox}]^+$ *m/z* 773.0 ($[Yb(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 773.0).

Other $[Ln(OTf)_3(Pr^i\text{-pybox})_2]$ complexes were prepared in a similar way.

$[La(OTf)_3(Pr^i\text{-pybox})_2]$. FAB mass spectrum: $[M - OTf]^+$ *m/z* 1039.2 ($[La(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 1039.2); $[M - OTf - (Pr^i\text{-pybox})]^+$ *m/z* 773.0 ($[La(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 773.0).

$[Nd(OTf)_3(Pr^i\text{-pybox})_2]$. FAB mass spectrum: $[M - OTf]^+$ *m/z* 1044.1 ($[Nd(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 1042.2); $[M - OTf - (Pr^i\text{-pybox})]^+$ *m/z* 742.9 ($[Nd(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 741.0).

$[Eu(OTf)_3(Pr^i\text{-pybox})_2]$. FAB mass spectrum: $[M - OTf]^+$ *m/z* 1053.2 ($[Eu(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 1053.2); $[M - OTf - (Pr^i\text{-pybox})]^+$ *m/z* 751.8 ($[Eu(OTf)_2(Pr^i\text{-pybox})_2]^+$ = 752.0).

***rac*-$[La(OTf)_3(Pr^i\text{-pybox})_2]$.** FAB mass spectrum: $[M - OTf]^+$ *m/z* 1039; $[M - OTf - (Pr^i\text{-pybox})]^+$ *m/z* 737.8.

***rac*-$[Yb(OTf)_3(Pr^i\text{-pybox})_2]$.** FAB mass spectrum: $[M - OTf]^+$ *m/z* 1074.2; $[M - OTf - (Pr^i\text{-pybox})]^+$ *m/z* 773.0.

General Method for $[LnCl_3(pybox)_2]$-Catalyzed Silylcyanation Reactions. A solution of Pr^i-pybox (0.054 g, 1.8 mmol) in dry MeCN (10 cm^3) was added to anhydrous $LnCl_3$ (0.09 mmol). The reaction mixture was stirred at room temperature for 1 h, resulting in a clear, colorless solution. The solution was cooled to 0 °C, and then aldehyde (2.14 mmol) was added, followed by TMSCN (285 μL, 2.14 mmol). Stirring at 0 °C was continued for 90 min. A portion of 1 M HCl (10 cm^3) was added, and the reaction mixture was warmed to room temperature. Product was extracted into Et_2O (50 cm^3), dried (Na_2SO_4), and concentrated to give crude cyanohydrin.

Determination of Enantiomeric Excess of Cyanohydrins.[45] Cyanohydrin (0.15 mmol) was dissolved in toluene (3 cm^3). (1R,2S,5R)-(−)-menthyl chloroformate (70 μL, 0.33 mmol) and pyridine (40 μL, 0.5 mmol) were added, and the reaction mixture was stirred overnight at room temperature. Volatiles were removed in vacuo, and the product was analyzed by ^1H NMR spectroscopy. Integration of the signal due to the proton α to the cyano group gave the enantiomeric excess.

Crystallographic Studies. All X-ray data were collected at 213(2) K using a Bruker-AXS Smart Apex CCD diffrac-

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(40) Evans, W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797–802.

(41) Knoeppel, D. W.; Liu, J. P.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 4828–4837.

(42) Ryu, D. H.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8106–8107.

(43) Carter, C. P.; Taylor, M. D. *J. Inorg. Nucl. Chem.* **1962**, *24*, 387.

(44) Nishiyama, H.; Kondo, M.; Nakamura, T.; Itoh, K. *Organometallics* **1991**, *10*, 500–508.

(45) Brunel, J. M.; Legrand, O.; Buono, G. *Tetrahedron: Asymmetry* **1999**, *10*, 1979–1984.

Table 5. Crystallographic Data

	[YbCl$_2$(*S*-Pr^i-pybox)$_2$]-[YbCl$_4$(*S*-Pr^i-pybox)]·3MeCN	[EuCl$_2$(*S*-Pr^i-pybox)$_2$]-[EuCl$_4$(*S*-Pr^i-pybox)]·2MeCN	[La(OTf)$_3$(*S*-Pr^i-pybox)$_2$].THF
formula	$C_{54}H_{69}Cl_6N_{12}O_6Yb_2$	$C_{55}H_{72}Cl_6Eu_2N_{11}O_6$	$C_{41}H_{54}F_9LaN_6O_{14}S_3$
formula wt	1462.93	1499.86	1260.99
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$C2$	$P2_12_12_1$
Z	4	4	4
a, Å	15.0756(7)	48.157(7)	12.9384(14)
b, Å	48.534(2)	9.5111(14)	18.489(2)
c, Å	9.6438(4)	15.123(2)	22.340(5)
α, deg	90	90	90
β, deg	90	98.601(2)	90
γ, deg	90	90	90
V, Å^3	7056.2(5)	6848.7(17)	5343.9(14)
$d_{\text{calcd.}}$, g cm^{-3}	1.377	1.455	1.567
GOF (F^2)	1.117	1.125	0.963
R1	0.0635	0.0539	0.0383

tometer (Mo Kα, graphite monochromator) in the ϕ rotation scan mode. The structures were solved by direct methods with the SHELXS97 package and refined using full-matrix least squares on F^2 (SHELXL97). Absolute structures of [La(OTf)$_3$(*S*-Pr^i-pybox)$_2$], [YbCl$_2$(*S*-Pr^i-pybox)$_2$][YbCl$_4$(*S*-Pr^i-pybox)], [EuCl$_2$(*S*-Pr^i-pybox)$_2$][EuCl$_4$(*S*-Pr^i-pybox)], and [Yb(OTf)$_2$(*S*-Pr^i-pybox)$_2$][OTf] were determined from the values of the Flack parameter. Crystallographic data are summarized in Table 5.

[Ln(OTf)$_3$(Pr^i-pybox)$_2$]·THF. Single crystals were grown at 4 °C from concentrated THF solutions by slow diffusion of Et$_2$O.

[LnCl$_2$(Pr^i-pybox)$_2$][LnCl$_4$(Pr^i-pybox)]. Single crystals were grown at −18 °C by slow diffusion of Et$_2$O into a concentrated MeCN solution.

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Supporting Information Available: CIF files for the compounds [La(OTf)$_3$(*S*-Pr^i-pybox)$_2$], [YbCl$_2$(*S*-Pr^i-pybox)$_2$][YbCl$_4$(*S*-Pr^i-pybox)], [EuCl$_2$(*S*-Pr^i-pybox)$_2$][EuCl$_4$(*S*-Pr^i-pybox)], [Yb(OTf)$_2$(*S*-Pr^i-pybox)$_2$][OTf], and [Eu(OTf)$_2$(H$_2$O)(*S*-Pr^i-pybox)(*R*-Pr^i-pybox)][OTf], a table giving crystallographic data collection details for [Yb(OTf)$_2$(*S*-Pr^i-pybox)$_2$][OTf] and [Eu(OTf)$_2$(H$_2$O)(*S*-Pr^i-pybox)(*R*-Pr^i-pybox)][OTf], and text giving experimental details for the preparation of Pr^i-pybox. This material is available free of charge via the Internet at http://pubs.acs.org.

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