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Solubilized Lanthanide Triflates: Lewis Acid Catalysis by Polyether and Poly(ethylene glycol) Complexes of Ln(OTf)$_3$

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Complexes of lanthanide triflates Ln(OTf)$_3$ with polyether (MeO(CH$_2$CH$_2$O)$_n$Me) and poly(ethylene glycol) (HO(CH$_2$CH$_2$O)$_n$H) ligands (n = 2−4) have been prepared and characterized, and the activity of these complexes as Lewis acid catalysts has been investigated. The complexes [Ln(OTf)$_3$(HO(CH$_2$CH$_2$O)$_n$H)] have been shown to catalyze the allylation of a range of aldehydes with allyltributylstannane, and the complexes [Ln(OTf)$_3$(MeO(CH$_2$CH$_2$O)$_n$Me)] catalyze the Diels−Alder addition of *N*-crotonyloxazolidinone to cyclopentadiene. The single-crystal X-ray structures of [Dy(OTf)$_2$(H$_2$O)$_2$(MeO(CH$_2$CH$_2$O)$_4$Me)][OTf] and [La(OTf)$_3$(THF)(HO(CH$_2$CH$_2$O)$_4$H)] are reported.

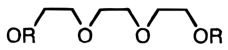
Introduction

The use of lanthanide triflates Ln(OTf)$_3$ (OTf = CF$_3$SO$_3$) as Lewis acid catalysts was first reported in 1991,[1] and since that date these compounds have been applied successfully to the catalysis of a wide range of important organic transformations, for example the Michael reaction,[2] the Diels−Alder reaction,[3] Friedel−Crafts acylation,[4] and carbonyl allylation.[5] Lanthanide triflates are now commercially available, and their use in organic synthesis has recently been reviewed.[6] The development of enantioselective versions of these reactions is an important goal, but if this is to be achieved in a rational way, the coordination chemistry of Ln(OTf)$_3$ must be better understood and the effect on catalytic activity of altering the coordination sphere must be evaluated. Despite the growing interest in the application of Ln(OTf)$_3$ in catalysis, very little is known about the coordination chemistry of these salts, and in no case has the catalytically active species been characterized. In this work we describe the preparation of soluble polyether and poly(ethylene glycol) complexes of Ln(OTf)$_3$ and compare their catalytic activity with that of Ln(OTf)$_3$ in two important C−C bond-forming reactions: the carbonyl allylation reaction (reaction 1) and the Diels−Alder reaction (reaction 2).

Results and Discussion

Lanthanide ions are highly oxophilic, and their salts are notoriously difficult to obtain in an anhydrous state. The [Ln(H$_2$O)$_9$]$^{3+}$ ion is very readily formed and has been shown to be present in crystalline hydrated Ln(OTf)$_3$.[7] Anhydrous lanthanide salts are polymeric and are generally insoluble in noncoordinating solvents, however anhydrous, soluble molecular complexes may be prepared with poly(ethylene glycol) or polyether ligands, and such complexes have been reported for lanthanide nitrates and chlorides.[8−11] These acyclic analogues of the crown ethers are attractive ligands, not only because of their low cost and ready commercial availability but also because their flexibility gives them the ability to coordinate to a wider range of metal centers than do the crown ethers. The chelating polyether ligand may bind strongly enough to the Ln^{3+} ion to displace coordinated H$_2$O ligands and thus provide a facile route to anhydrous Ln salts. We therefore chose to begin our investigation of coordination chemistry of Ln(OTf)$_3$ with the ligands below:

R=H; diethyleneglycol; EO$_2$
R=Me; diglyme; M$_2$EO$_2$



R=H; triethyleneglycol; EO$_3$
R=Me; triglyme; M$_2$EO$_3$

R=H;tetraethyleneglycol; EO$_4$
R=Me; tetraglyme; M$_2$EO$_4$

Complexes with poly(ethylene glycol) ligands (**1**−**3**, R = H) and with polyether ligands (**1**−**3**, R = Me) were

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[1] Kobayashi, S. *Chem. Lett.* **1991**, 2087.

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[3] Kobayashi, S.; Hachiya, I.; Takahori, T.; Araki, M.; Ishitani, H. *Tetrahedron Lett.* **1992**, *33*, 6815.

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[6] (a) Marshman, R. W. *Aldrichim. Acta* **1995**, *28*, 77. (b) Kobayashi, S. *Synlett* **1994**, 689.

[7] Harrowfield, J. M.; Weimin, L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1994**, *47*, 339.

[8] Hirashima, Y.; Shiokawa, J. *Chem. Lett.* **1979**, 453.

[9] Hirashima, Y.; Tsutsui, T.; Shiokawa, J. *Chem. Lett.* **1981**, 1501.

[10] Casellato, U.; Tomat, G.; di Bernadino, P. *Inorg. Chim. Acta* **1982**, *61*, 181.

[11] Rogers, R. D.; Etzenhouser, R. D.; Murdoch, J. S.; Reyes, E. *Inorg. Chem.* **1991**, *30*, 1445.

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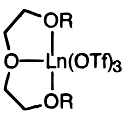
Table 1. FAB Mass Spectra (*m*/*e*) for $[Ln(OTf)_3(M_2EO_n)]$

	n	$[Ln(OTf)_2(M_2EO_n)]^+$	$[Ln(OTf)(M_2EO_n)F]^+$	$[Ln(M_2EO_n)F_2]^+$
La	4	659	529	399
Dy	4	684	554	
Yb	4	694	564	434
Y	4	609	479	349
La	3	615	485	355
Y	3	650	520	390
Yb	3	565	435	305
Y	2	521	391	261

Table 2. FAB Mass Spectra (*m*/*e*) for $[Ln(OTf)_3(EO_n)]$

Ln	*n*	$[Ln(OTf)_2(EO_n)]^+$	$[Ln(OTf)(EO_n) - H]^+$
La	4	631	481
Yb	4	666	516
Y	4	581	431
La	3	587	437
Y	3	622	472
Yb	3	537	387
La	2	543	393
Y	2	578	428
Yb	2	493	343

prepared for several lanthanides in order to cover a range of Ln^{3+} radius from large (La^{3+}) to small (Yb^{3+}).



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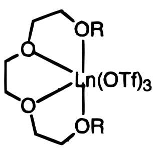

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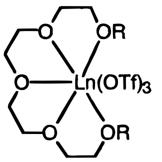

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Choice of Complexes for Study. We have chosen to investigate a range of Ln from La (large ionic radius) to Yb (small ionic radius), and ligands with three, four, or five O donor atoms in order to study the effect of ionic radius and coordination number on the catalytic activity of $Ln(OTf)_3$ complexes. We have paid particular attention to complexes with the pentadentate ligands tetraglyme and tetrakis(ethylene glycol), as we believe that the large size of the lanthanides, and the lability of most of their complexes, will require the use of multidentate ligands for the synthesis of stable homochiral complexes suitable for enantioselective catalysis.

Preparation and Characterization of the Complexes. $[Ln(OTf)_3(M_2EO_n)]$ and $[Ln(OTf)_3(EO_n)]$ were prepared by addition of 1 equiv of the appropriate M_2EO_n or EO_n to a CH_2Cl_2 solution of $Ln(OTf)_3.nH_2O$. Addition of petroleum ether to these reaction solutions resulted in precipitation of the hydrated complexes $[Ln(OTf)_2(H_2O)_2(M_2EO_4)][OTf]$. Anhydrous complexes were prepared by azeotropic distillation of the reaction solution for 3 h through a Soxhlet extractor containing 4 Å molecular sieves, followed by precipitation by addition of petroleum ether. Heating the hydrated complexes to ca. 90−100 °C at 10^{-2} mmHg also yielded the anhydrous complexes. All new complexes were characterized by FAB mass spectrometry (see Tables 1 and 2); the M_2EO_n complexes all showed similar fragmentation patterns and the major peaks were assigned to $[M - (OTf)]^+$, $[M - (OTf)_2 + F]^+$ and $[M - (OTf)_3 + 2F]^+$; the EO_n complexes gave rise to peaks due to $[M - (OTf)]^+$ and $[M - (OTf)_2 - H]^+$. Combustion analysis for C and H was not carried out due to the high F content (>20%).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Dy(OTf)_2(H_2O)_2(M_2EO_4)$ and $[La(OTf)_3((thf)(EO_4)]$

$[Dy(OTf)_2(H_2O)_2(M_2EO_4)]$		$[La(OTf)_3(THF)(EO_4)]$	
Dy−O1	2.492(9)	La−O1	2.547(4)
Dy−O2	2.441(9)	La−O2	2.604(4)
Dy−O3	2.503(7)	La−O3	2.617(4)
Dy−O4	2.434(8)	La−O4	2.583(4)
Dy−O5	2.456(8)	La−O5	2.569(4)
Dy−O6	2.432(8)	La−O11	2.486(4)
Dy−O7	2.411(9)	La−O21	2.481(4)
Dy−O12	2.378(8)	La−O31	2.488(4)
Dy−O13	2.342(8)	La−O6	2.564(4)
O1−Dy−O2	65.4(3)	O1−La−O2	63.0(1)
O2−Dy−O3	63.6(3)	O2−La−O3	62.0(1)
O3−Dy−O4	66.4(3)	O3−La−O4	63.9(1)
O4−Dy−O5	65.4(3)	O4−La−O5	61.5(1)

The IR spectra of hydrated complexes all showed absorptions at ca. 3400 and 1645 cm^{-1} due to coordinated H_2O as well as a sharp absorption at 1028 cm^{-1} characteristic of uncoordinated OTf^-. These absorptions were absent in the spectra of complexes dried for 4 h at 90−100 °C and 10^{-2} mmHg; these conditions were subsequently used for the preparation of anhydrous complexes for catalytic studies. IR spectra of dried $[Ln(OTf)_3(EO_n)]$ all showed single absorptions at ca. 3340−3370 cm^{-1} due to coordinated OH of the EO_n ligand.

Crystallographic Studies. Complexes of lanthanides with polyether and poly(ethylene glycol) ligands are well-known, but until now no such complexes with OTf^- ligands have been reported. Complexes of $La(OTf)_3$ with 18-crown-6 and with a perfluoroalkyl derivative of this crown ether have been reported recently but have not been investigated for catalytic activity.[12] We have characterized crystallographically one complex, $[Dy(OTf)_2(H_2O)_2(M_2EO_4)][OTf]$, with the M_2EO_4 ligand and one complex, $[La(OTf)_3(THF)(EO_4)]$, with the EO_4 ligand. Table 3 summarizes important bond distances and angles for complexes.

The anhydrous polyether complexes $[Ln(OTf)_3(M_2EO_4)]$ yielded badly disordered crystals from CH_2Cl_2/petroleum ether, and although a data set was collected for Ln = Y, we were unable to refine the structure adequately for publication. The unit cell parameters for this complex are given in the Experimental Section. However, the hydrated complex $[Dy(OTf)_2(H_2O)_2(M_2EO_4)][OTf]$ gave good-quality crystals from CH_2Cl_2/petroleum ether and the molecular structure was determined; an ORTEP plot is shown in Figure 1. This nine-coordinate complex has an irregular geometry in which five coordination sites are occupied by the O donors of M_2EO_4; the remaining sites are occupied by two OTf^- groups and two H_2O molecules. The Dy atom is displaced by 0.087 Å from the least−squares plane defined by the five O donors of M_2EO_4; the mean displacement of O atoms from this plane is 0.582 Å. OTf^- is a poor nucleophile, and it is probable that in the catalytic reactions it is displaced from the coordination sphere of the lanthanide by the carbonyl groups of the organic substrates to produce a charged intermediate. The average Dy−O(water) distance of 2.36(2) Å is close to the average Dy−O(triflate) distance of 2.42(1)

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(12) Chen, J.; Zhang, Y.-F.; Zheng, X.; Vij, A.; Wingate, D.; Meng, D.; White, K.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg., Chem.* **1996**, *35*, 1590.

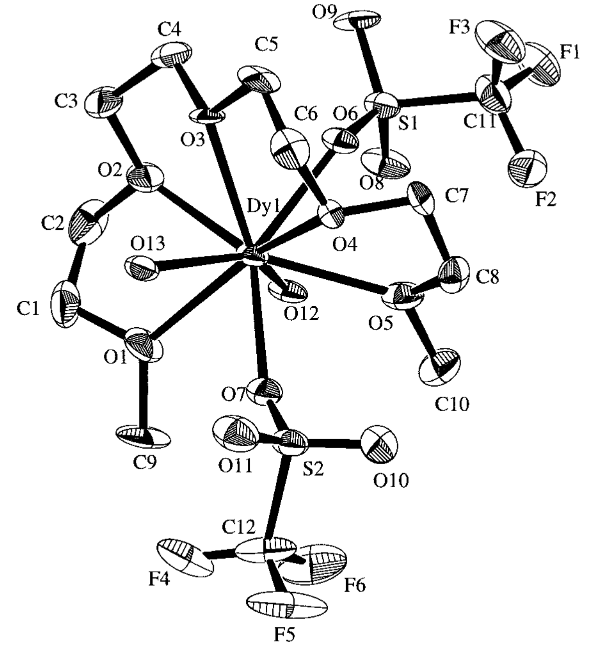


Figure 1. ORTEP plot (at the 50% probability level) of $[Dy(OTf)_2(H_2O)_2(M_2EO_4)]^+$. Selected geometrical data are given in Tables 3 and 4.

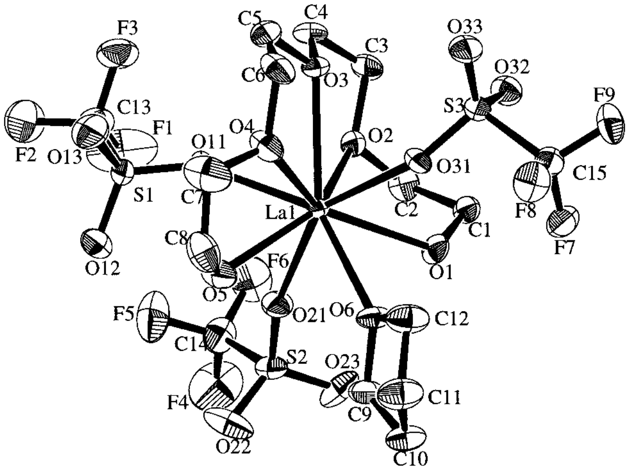


Figure 2. ORTEP plot (at the 50% probability level) of $[La(OTf)_3(THF)(EO_4)]$. Selected geometrical data are given in Tables 3 and 4.

Å; in $[La(OTf)_2(H_2O)_2(18\text{-}C\text{-}6)]^+$ the average La–O(water) distance (2.544(1) Å) is significantly *longer* than the average La–O(triflate) distance of 2.506(2) Å.[12]

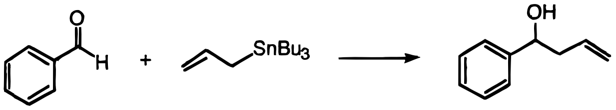
The $[Ln(OTf)_3(EO_n)]$ complexes were somewhat less soluble in CH_2Cl_2 than the corresponding M_2EO_n complexes, and we were unable to obtain crystals suitable for diffraction from this solvent. Good-quality crystals of $[La(OTf)_3(THF)(EO_4)]$ were obtained from THF/petroleum ether and an ORTEP plot of this complex is shown in Figure 2. This nine-coordinate complex has an irregular geometry in which five coordination sites are occupied by the O donors of EO_4; the remaining sites are occupied by three OTf^- groups and one THF molecule. The La atom is displaced by 0.046 Å from the least-squares plane defined by the five O donors of EO_4; the mean displacement of O atoms from this plane is 0.662 Å. The average La–OH distance of 2.56(1) Å is only very slightly shorter than the average La–O(ether) distance of 2.60(1) Å.

Table 4. Catalysis of the Allylation of Benzaldehyde[a]

cat.	amt, mol %	time	amt of product (R = Ph), %
fresh $Yb(OTf)_3$	5	90 min	100
1 yr old $Yb(OTf)_3$	5	90 min	48
$[Yb(OTf)_3(EO_4)]$	10	4 h	77
$[Yb(OTf)_3(EO_4)]$	10	24 h	94
$[La(OTf)_3(EO_4)]$	10	24 h	86
$[Yb(OTf)_3(EO_2)]$	10	4 h	85
$[Yb(OTf)_3(EO_2)]$	10	24 h	96

[a] Vacuum-dried catalyst in dry CH_2Cl_2 at room temperature. The percentage of the product was determined by ^1H NMR spectroscopy of the quenched reaction mixture.

Catalytic Activity of the Complexes. (i)Allylation of Aldehydes with Allyltributyltin. Reaction 1 is a useful C–C bond-forming reaction which may be promoted by stoichiometric quantities of traditional Lewis acids such as $TiCl_4$; we recently reported the efficient catalysis of this reaction by $Yb(OTf)_3$.[5] $[Ln(OTf)_3(M_2EO_n)]$ species (Ln = La, Y, Yb) were found *not* to catalyze the desired reaction, but instead they catalyzed complex side reactions to give numerous as yet uncharacterized products. The side reactions were supressed in the presence of H_2O, but the rate of the desired carbonyl allylation was very slow under these conditions. This suggested to us that an OH group coordinated to the Ln was necessary for the reaction to proceed as desired and we therefore investigated catalysis by complexes with EO_n ligands. We indeed found that all the $[Ln(OTf)_3(EO_n)]$ complexes were effective catalysts for the allylation reaction. As expected, we found that for a particular EO_n, the most active catalyst is the complex with the small Yb^{3+} ion. The smaller EO_n ligands give the most active catalysts, presumably because these complexes are the most coordinatively unsaturated. Some results for the allylation of benzaldehyde (reaction 1; R = Ph) are summarized in Table 4. It is noteworthy that $Yb(OTf)_3$ is subject to an aging process and is significantly less active after 1 year than freshly prepared material, even when both are subjected to the same drying procedure. There is no loss of activity with age in the poly(ethylene glycol) complexes: samples over 18 months old have been successfully used in catalytic reactions.



(1)

Due to the large ionic radii of the lanthanides, it is likely that tetra- or pentadentate ligands will be required to produce a stable chiral complex and we therefore concentrated most of our attention on the catalytic activity of $[Yb(OTf)_3(EO_4)]$ as a model complex. We have now extended the range of substrates to which this carbonyl allylation may be applied, and the results are summarized in Table 5.

(ii) Diels–Alder Reaction. Catalysis of the Diels–Alder addition of *N*-crotonyloxazolidinone to cyclopentadiene (reaction 2) has been well studied,[13] and an

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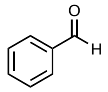
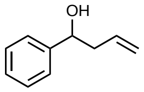
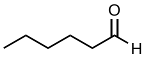
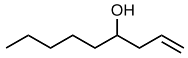
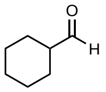
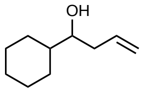
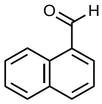
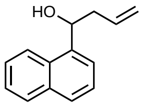
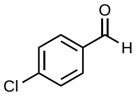
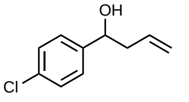
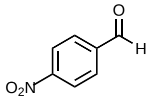
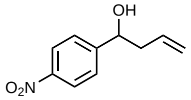
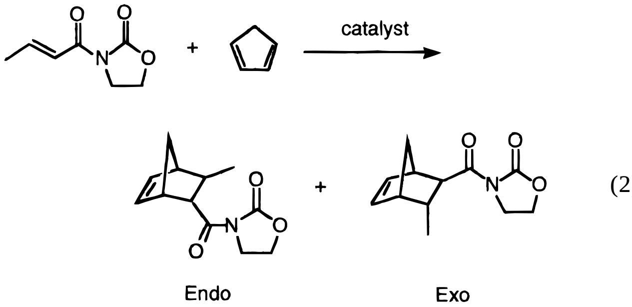
[13] Kobayashi, S.; Hachiya, I.; Araki, M.; Ishitani, H. *Tetrahedron Lett.* **1993**, *34*, 3755.

Table 5. Scope of the Carbonyl Allylation Reaction Catalyzed by [Ln(OTf)$_3$(EO$_4$)]^a

substrate	product	isolated yield, %
		85
		89
		90
		70
		77
		78

^{a} Conditions: 10 mol % vacuum-dried catalyst, CH$_2$Cl$_2$, 24 h, room temperature.

enantioselective version of the reaction has been developed.[14,15] We therefore chose this system for initial catalytic studies with our complexes so that useful comparisons may be made. Because of our ultimate aim of preparing enantioselective catalysts, we have concentrated our attention on complexes of pentadentate ligands as models for stable homochiral catalysts. Results are summarized in Table 6.



(2)

As expected, in the series of [Ln(OTf)$_3$(M$_2$EO$_4$)] compounds the La complex showed the poorest activity (no reaction observed at 0 °C), and it also showed the poorest selectivity. [Y(OTf)$_3$(M$_2$EO$_4$)] and [Yb(OTf)$_3$(M$_2$EO$_4$)] both showed similar activity and better selectivity than Yb(OTf)$_3$, comparable to those reported for Sc(OTf)$_3$, which is far more expensive.[13] We found that the catalytic activity and selectivity of [Yb(OTf)$_3$(M$_2$EO$_4$)] were undiminished when the complex was not dried, whereas Yb(OTf)$_3$ was inactive under these conditions. The poly(ethylene glycol) complex [Yb(OTf)$_3$(EO$_4$)] was found to be very much poorer in terms of both activity and selectivity than [Yb(OTf)$_3$(M$_2$EO$_4$)].

Conclusions

In summary, we have prepared complexes of lanthanide triflates with a series of polyether and poly(ethylene glycol) ligands and investigated their catalytic activity in two impoprtant C−C bond-forming reactions. The complexes show improved handling properties (enhanced solubility, ease of drying) compared with the parent Ln(OTf)$_3$. The poly(ethylene glycol) complexes are effective catalysts for the carbonyl allylation reaction, although, as expected, the coordination of O-donor ligands leads to some reduction in catalytic activity for these complexes when compared with the parent Ln(OTf)$_3$. The polyether complexes catalyze the Diels−Alder reaction with activities and selectivities rivaling those of the much more expensive Sc(OTf)$_3$; in this case coordination of the polyether ligand leads to enhancement of selectivity and *no* reduction in catalytic activity when compared with the parent Ln(OTf)$_3$. Complexes of Ln(OTf)$_3$ with homochiral polyether and poly(ethylene glycol) ligands are now under investigation.[16]

Table 6. Catalysis of the Diels−Alder Reaction of Cyclopentadiene with *N*-Crotyloxazolidinone^a

cat.	amt, mol %	temp, °C	time, h	isolated yield, %	exo:endo
[La(OTf)$_3$(M$_2$EO$_4$)]^b	10	0	13	no reacn	
[La(OTf)$_3$(M$_2$EO$_4$)]^b	10	20	60	84	1:1.2
[Y(OTf)$_3$(M$_2$EO$_4$)]	20	0	23	76	1:3
[Y(OTf)$_3$(M$_2$EO$_4$)]	11	0	21	73	1:5.1
[Y(OTf)$_3$(M$_2$EO$_4$)]	2	0	49	66	1:5.0
[Yb(OTf)$_3$(M$_2$EO$_4$)]	10	0	21	77	1:4.7
[Yb(OTf)$_3$(M$_2$EO$_4$)]^c	10	0	22	80	1:5.2
[Yb(OTf)$_3$(EO$_4$)]	10	20	528	57	1:1.8
Yb(OTf)$_3$	10	0	24	67	1:3
Yb(OTf)$_3$^{c}	10	20	100	no reacn	
Sc(OTf)$_3$^{d}	10	0	12	97	1:5.2

^{a} Unless otherwise stated, the catalyst was dried before use and the reaction was conducted under anhydrous conditions. ^{b} Catalyst prepared in situ by addition of M$_2$EO$_4$ to dried Ln(OTf)$_3$ in CH$_2$Cl$_2$. ^{c} Neither catalyst nor solvent was dried before use. ^{d} Reference 13.

Experimental Section

In cases where rigorously anhydrous conditions are specified, standard Schlenk techniques were employed. Solvents were distilled under N$_2$ from sodium benzophenone ketyl (THF) or CaH$_2$ (CH$_2$Cl$_2$, petroleum ether) and stored over 4 Å molecular sieves prior to use. Benzaldehyde was purified by washing with saturated Na$_2$CO$_3$ followed by vacuum distillation, and was stored under N$_2$ prior to use. Ln(OTf)$_3$.nH$_2$O was prepared by reaction of HOTf with an excess of Ln$_2$O$_3$ in H$_2$O. Some heating was required in the case of Y, Dy, and Yb. Unreacted Ln$_2$O$_3$ was separated by filtration, and the filtrate was evaporated to yield Ln(OTf)$_3$.nH$_2$O as a crystalline solid.

Preparation of [Ln(OTf)$_3$(EO$_n$)] and [Ln(OTf)$_3$(M$_2$EO$_n$)]. Ln(OTf)$_3$.nH$_2$O (6 mmol) was dissolved in CH$_2$Cl$_2$ (150 cm^3). The appropriate M$_2$EO$_n$ or EO$_n$ (6 mmol) was then added. A Soxhlet extractor containing activated 4 Å molecular sieves was placed in the top of the reaction flask, and the reaction mixture was heated to reflux under N$_2$ for 3−4 h. Some product began to precipitate out of the solution (especially for the EO$_n$ complexes) after this time. Complete precipitation of product was effected by addition of petroleum ether. The product was isolated by filtration and dried in vacuo. Typical isolated yield: 85%.

General Procedure for Allylation of Aldehydes with Allyltributyltin. The allylation of benzaldehyde is described here; the procedure is analogous for other aldehydes.

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[Yb(OTf)$_3$(EO$_4$)] (0.32 mmol) was dried at 90−100 °C and 10^{-2} mmHg for 4 h. Dry CH_2Cl_2 (5 cm^3) was added, followed by PhCHO (3.25 mmol) and allyltributyltin (3.55 mmol). The reaction mixture was stirred at room temperature for 24 h. After this time, solvent was removed in vacuo from the reaction mixture, and sodium cyanoborohydride (3.5 mmol) and *tert*-butyl alcohol (10 cm^3) were added.[17] The resulting mixture was heated to reflux for 60 min, after which solvent was removed in vacuo. The resulting white oil was purified by flash chromatography (eluent petroleum ether/diethyl ether 9:1) to yield 1-phenyl-3-buten-1-ol as a colorless oil (85%; bp 78−80 °C, 0.15 mmHg). ^{1}H NMR ($CDCl_3$; 250 MHz; δ): 2.23 (1H, m); 2.46 (2H, m); 4.71 (1H, m); 5.10 (2H, m); 5.15 (1H, m); 5.19 (1H, m); 5.80 (1H, m); 7.20−7.60 (5H, m).

General Procedure for the Diels−Alder Reaction of Cyclopentadiene with *N*-Crotyloxazolidinone. A solution of *N*-crotonyloxazolidinone (100 mg, 0.65 mmol) in CH_2Cl_2 (2.5 cm^3) was added to an approriate quantity of dried catalyst in a 25 cm^3 Schlenk flask. This solution was stirred at 0 °C for 30 min, after which time freshly distilled cyclopentadiene (220 μL, 2.59 mmol) was added. The reaction mixture was stirred at 0 °C, with monitoring by TLC throughout. The reaction was quenched by addition of H_2O (5 cm^3), the aqueous layer was extracted into Et_2O (3 × 7 cm^3), and the combined organic extracts were dried ($MgSO_4$). Solvent was removed in vacuo, and the diastereoselectivity was determined by ^{1}H NMR spectroscopy (CH_3 (endo) δ 1.12, d, $J = 7.1$ Hz; CH_3(exo) δ 0.85, d, $J = 6.6$ Hz). Products were purified by flash chromatography (eluent CH_2Cl_2).

X-ray Crystallographic Studies. Crystals for low-temperature data collection were coated in Nujol oil and frozen onto glass fibers under a stream of N_2 gas at −120 °C. Crystals of [Dy(OTf)$_2$(H$_2$O)$_2$(M$_2$EO$_4$)] were grown from CH_2Cl_2/petroleum ether without taking any precautions to exclude water. Crystals of [Y(OTf)$_3$(M$_2$EO$_4$)] were grown from CH_2Cl_2/petroleum ether under rigorously anhydrous conditions. These crystals were disordered, and the structure of the complex could not be refined adequately. The following lattice parameters were obtained for [Y(OTf)$_3$(M$_2$EO$_4$)]: triclinic, space group $P\bar{1}$ (No. 2); $a = 13.036(8)$, $b = 13.83(1)$, $c = 10.218(7)$ Å; $\alpha = 105.66(6)$, $\beta = 110.94(5)$, $\gamma = 66.11(5)$°; $V = 1556(2)$ Å^3. Crystals of [La(OTf)$_3$(THF)(EO$_4$)] were grown from THF/petroleum ether under rigorously anhydrous conditions. Data were collected on a Rigaku AFC6S diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.710\,73$ Å). Structures were solved by direct methods using the TEXSAN package.[18] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions (d(C−H) = 0.95 Å) and were not refined. Crystallographic data are summarized in Table 7, and full experimental details are available in the Supporting Information.

Table 7. Crystal Data

	[Dy(OTf)$_2$(H$_2$O)$_2$-(M$_2$EO$_4$)]	[La(OTf)$_3$(THF)-(EO$_4$)]
empirical formula	$C_{13}H_{22}O_{16}F_9S_3Dy$	$C_{11}H_{18}O_{14}F_9S_3La$
fw	863.97	780.33
cryst syst	monoclinic	monoclinic
lattice params		
a, Å	17.334(1)	9.439(8)
b, Å	20.214(1)	15.420(6)
c, Å	8.131(1)	20.201(4)
β, deg	92.793(9)	93.44(3)
V, Å^3	2846(6)	2935(3)
space group (No.)	$P2_1/c$ (14)	$P2_1/c$ (14)
Z	4	4
D_{calc}, g/cm^3	2.016	1.766
no. of observns ($I > 3.00\sigma(I)$)	3412	3957
no. of variables	379	388
rfln/param ratio	9.00	10.19
residuals: R; R_w	0.057; 0.056	0.032; 0.039

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Supporting Information Available: Experimental details of the X-ray data collection including listings of positional and thermal paramameters, intramolecular bond distances and angles, and torsional angles (35 pages). Ordering information is given on any current masthead page.

OM9709087

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