ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 773–776

Journal of ALLOYS AND COMPOUNDS

New homochiral lanthanide(III) triflates in Lewis acid catalysis

Helen C. Aspinall*, Nicholas Greeves, Edward G. McIver

Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool, Liverpool L69 7ZD, UK

Abstract

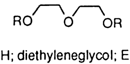
New complexes of lanthanide(III) triflates with polyethylene glycol ($HO(CH_2CH_2O)_nH$; n=2, 3, 4) and polyethyleneglycol dimethylether ($CH_3O(CH_2CH_2O)_nCH_3$; n=2, 3, 4) ligands have been prepared and characterised by X-ray diffraction. These complexes are effective Lewis acid catalysts for the allylation of aldehydes with allyltributyltin, and for the Diels–Alder reaction. Complexes with new homochiral podand ligands have been synthesised and in one case characterised by X-ray diffraction, and their catalytic activity is under investigation. © 1998 Elsevier Science S.A.

Keywords: Lanthanide triflate; Catalysis; Lewis acid; Allylation; Diels–Alder; Polyether

1. Introduction

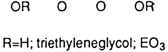
Lanthanide triflates have been shown to be versatile Lewis acid catalysts for a range of useful transformations; they are now commercially available and their applications have recently been reviewed [1]. Modification of the coordination sphere of the Lewis acid may lead to modified activity or selectivity, and modification with a chiral ligand is essential if the goal of enantioselective catalysis is to be achieved. The solution lability of most lanthanide complexes suggested to us that multidentate ligands would be required to form stable catalysts, and we therefore began our investigations with the readily available achiral polyether and polyethyleneglycol ligands (**1**), (**2**) and (**3**) to determine the effect on catalytic activity of coordination of these ligands to $Ln(OTf)_3$.

(1)



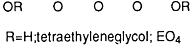
R=H; diethyleneglycol; EO_2
R=Me; diglyme; M_2EO_2

(2)

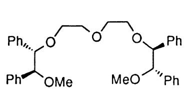


R=H; triethyleneglycol; EO_3
R=Me; triglyme; M_2EO_3

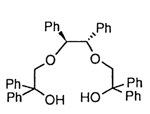
(3)



R=H;tetraethyleneglycol; EO_4
R=Me; tetraglyme; M_2EO_4



(4)



(5)

We have recently prepared a series of novel homochiral podand ligands including (**4**) and (**5**), which are analogues of the simple ligands (**2**) and (**3**) [2]. In the present paper we describe the coordination chemistry of $Ln(OTf)_3$ with polyether and polyethyleneglycol ligands, the Lewis acid catalytic activity of the resulting complexes, and some preliminary results with ligand (**4**).

2. Preparation of the complexes

Before embarking on the synthesis of new homochiral podand ligands it was important first to establish how the coordination of readily available achiral podands would affect the catalytic activity of $Ln(OTf)_3$. We began our investigations with the preparation of complexes with polyether and polyethyleneglycol ligands (**1**), (**2**) and (**3**). These complexes were readily prepared by addition of one equivalent of the appropriate ligand to a CH_2Cl_2 solution of hydrated $Ln(OTf)_3$. The solution was dried by azeotropic distillation through 4 Å molecular sieves in a Soxhlet extractor, and pure anhydrous product was precipitated out in high yield from the reaction solution by addition of petroleum ether. The complexes were characterised by FAB mass spectrometry, IR spectroscopy and in two cases by X-ray diffraction. The complexes were slightly hygroscopic and on exposure to air they absorbed H_2O to yield complexes of the type $[Ln(OTf)_m(L)(H_2O)_n][OTf]_{3-m}$, the IR spectra of which showed the presence of coordinated H_2O and uncoordinated OTf^-. These hydrated complexes were easily dehydrated by heating under vacuum to ca. 90°C for 1 h, much milder conditions than those required to dehydrate $Ln(OTf)_3 \cdot nH_2O$.

Good quality crystals of $[La(OTf)_3(THF)(EO_4)]$ were

---

*Corresponding author.

0925-8388/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(98)00438-1

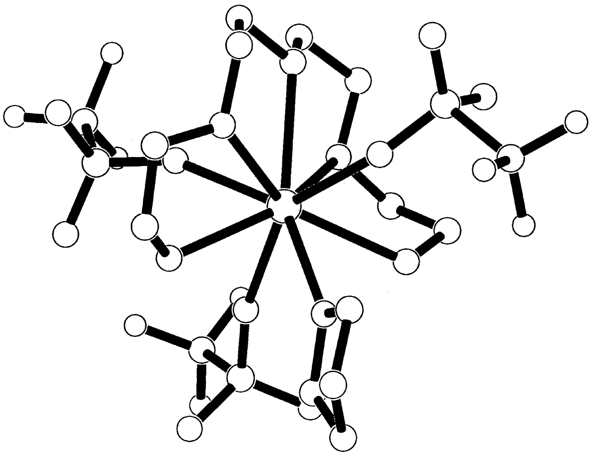


Fig. 1. Structure of [La$(OTf)_3$(THF)(EO_4)].

obtained from THF/petroleum ether, and [Dy$(OTf)_2(H_2O)_2(M_2EO_4)$][OTf] was crystallised from CH_2Cl_2/petroleum ether. Both these complexes were characterised by single-crystal X-ray diffraction; diagrams of their structures are shown in Figs. 1 and 2, respectively. In both these structures OTf^- acts as a monodentate ligand and the Ln ion lies very close to the least squares plane defined by the five O atoms of the podand ligand. Crystals of [Ln$(OTf)_3(M_2EO_4)$] (Ln=La, Y, Yb) were unfortunately badly disordered and unsuitable for X-ray diffraction.

Complexes with the homochiral ligands (**4**) and (**5**) were prepared in an analogous manner; they were found to be extremely soluble in organic solvents, and could be crystallised from toluene/petroleum ether. These complexes were much less hygroscopic than those with the simple polyether and polyethyleneglycol ligands. [Eu$(OTf)_3$(**4**)] was characterised by X-ray diffraction; a diagram of its structure is shown in Fig. 3. The conformation of the homochiral polyether ligand is very similar to that of the M_2EO_4 ligand in achiral analogues, with the Eu atom lying just 0.3 Å out of the least-squares plane defined by the five O donors.

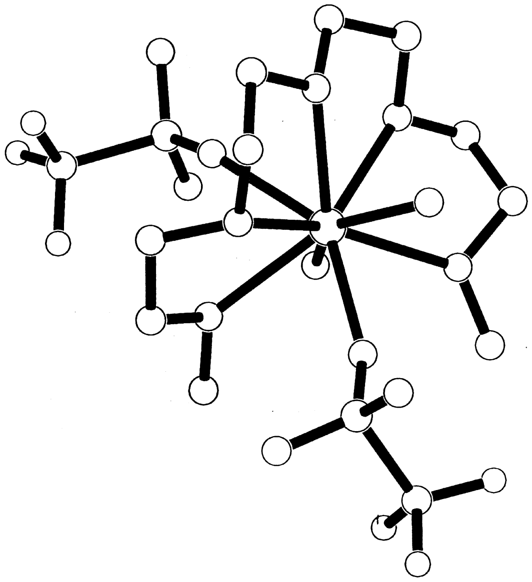


Fig. 2. Structure of [Dy$(OTf)_2(H_2O)_2(M_2EO_4)$][OTf]. The uncoordinated OTf^- has been omitted for clarity.

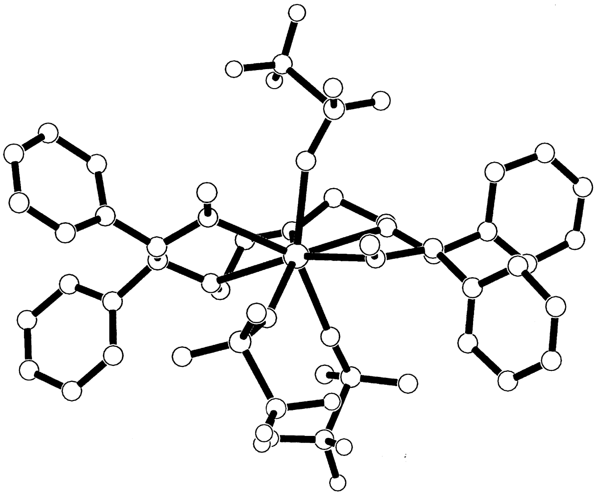
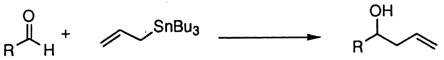


Fig. 3. Structure of [Eu$(OTf)_3$(**4**)].

3. Catalytic activity of the complexes

3.1. Allylation of aldehydes with allyltributyltin

Reaction (1) below 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$(OTf)_3$ [3].



Reaction 1

[Ln$(OTf)_3(M_2EO_n)$] (Ln=La, Y, Yb) were found *not* to catalyse the desired reaction, but instead they catalysed complex side reactions to give as yet uncharacterised 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 was the complex with Yb. The smaller EO_n ligands gave 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 summarised in Table 1.

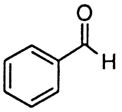
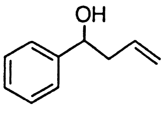
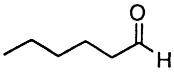
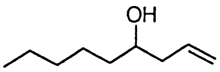
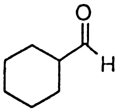
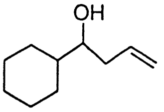
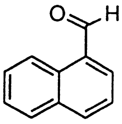
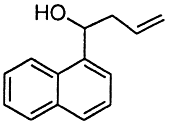
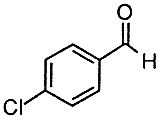
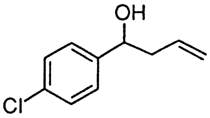
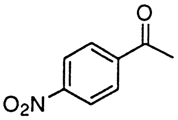
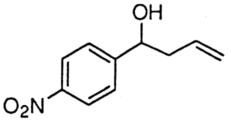
Due to the large ionic radii of the lanthanides it is likely

Table 1
Activity of [$Yb(OTf)_3(EO_n)$] in the allylation of benzaldehyde[a]

Catalyst	Mol%	Time	% product (R=Ph)
Fresh $Yb(OTf)_3$	5	90 min	100
1-year-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
[$Yb(OTf)_3(EO_2)$]	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. Yield determined by ^1H NMR of quenched reaction mixture.

Table 2
Scope of the carbonyl allylation reaction catalysed by [$Ln(OTf)_3(EO_4)$][a]

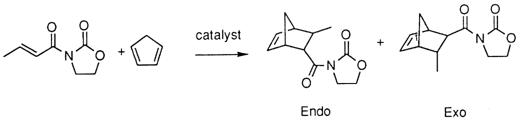
Substrate	Product	Isolated yield/%
		73
		89
		90
		70
		77
		78

[a] 10 mol% vacuum-dried catalyst, CH_2Cl_2, 24 h, room temperature.

that tetra- or pentadentate ligands will be required to produce a stable chiral complex and we therefore concentrated on 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 summarised in Table 2.

3.2. Diels–Alder reaction

The use of $Ln(OTf)_3$ and $Sc(OTf)_3$ as Lewis acid catalysts for the Diels–Alder reaction (2) below has been investigated by Kobayashi [4], as well as an asymmetric version [5], and we therefore chose this reaction for preliminary studies with our complexes.



Reaction 2

Our results are summarised in Table 3. As expected the La complex showed the poorest activity (no reaction observed at 0°C), and it also showed the poorest selectivity. Activity and selectivity were both better using [$Yb(OTf)_3(M_2EO_4)$] prepared in situ, but the best activity and selectivity we have so far obtained was achieved using 11 mol% of preformed [$Y(OTf)_3(M_2EO_4)$]. These results were better than those we obtained with 10 mol% of $Yb(OTf)_3$, and comparable to those reported by Kobayashi using the much more expensive $Sc(OTf)_3$ [4]. The polyethyleneglycol complex [$Yb(OTf)_3(EO_4)$] was found to be poorer in terms of activity and selectivity than [$Yb(OTf)_3(M_2EO_4)$].

4. Conclusions

We have prepared and characterised a series of lanthanide triflate complexes with readily available polyether and polyethyleneglycol ligands. These complexes show improved handling properties (enhanced solubility and ease of drying) compared with the parent $Ln(OTf)_3$. The

Table 3
Catalysis of Diels–Alder reaction (2)

Catalyst	Mol%	Temp. (°C)	Time (h)	Isolated yield (%)	Exo:Endo
[$La(OTf)_3(M_2EO_4)$][a]	20	20	60	84	1:1.2
[$Yb(OTf)_3(M_2EO_4)$][a]	20	0	21	80	1:2.5
[$Y(OTf)_3(M_2EO_4)$][b]	20	0	23	76	1:3
[$Y(OTf)_3(M_2EO_4)$][b]	11	0	21	73	1:5.1
[$Y(OTf)_3(M_2EO_4)$][b]	2	0	49	66	1:4.95
[$Y(OTf)_3(EO_4)$][b]	10	0	24	67	1:2.6
[$Eu(OTf)_3$(**4**)][b]	10	20	21	66	1:3
$Yb(OTf)_3$	10	0	24	67	1:3
$Sc(OTf)_3$[c]	10	0	12	97	1:5.2

[a] Catalyst prepared in situ by addition of M_2EO_4 to vacuum-dried $Ln(OTf)_3$.
[b] Preformed catalyst.
[c] See Ref. [4].

polyethyleneglycol complexes are versatile catalysts for the allylation of aldehydes with allyltributyltin and are not subject to the ageing process we have observed for Yb(OTf)$_3$. The polyether complexes are promising catalysts for the Diels–Alder reaction, showing enhanced activity and diastereoselectivity when compared with the parent Ln(OTf)$_3$. We have prepared and characterised stable homochiral lanthanide triflate complexes and investigations of their catalytic activity are in progress.

Acknowledgements

We are grateful to EPSRC for financial support (studentship to E.G.M), to Rhône-Poulenc for a gift of rare earth oxides, and to Miss J.L.M. Dwyer and Mr J.C. Woolley for preliminary work.

References

[1] R.W. Marshman, Aldrichim. Acta 28 (1995) 77.
[2] H.C. Aspinall, N. Greeves, W.-M. Lee, E.G. McIver, P.M. Smith, Tetrahedron Lett. (1997) 38 4679.
[3] H.C. Aspinall, A.F. Browning, N. Greeves, P. Ravenscroft, Tetrahedron Lett. 35 (1994) 4639.
[4] S. Kobayashi, I. Hachiya, M. Araki, H. Ishitani, Tetrahedron Lett. 34 (1993) 3755.
[5] S. Kobayashi, H. Ishitani, I. Hachiya, M. Araki, Tetrahedron 50 (1994) 11623.