ELSEVIER

Journal of Organometallic Chemistry 647 (2002) 205–215

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Symmetric and asymmetric samarium alkoxide derivatives of bridging sulfur biphenolate and binaphtholate ligands; synthetic, structural, and catalytic studies

Polly L. Arnold *, Louise S. Natrajan, Jonathan J. Hall, Stephan J. Bird, Claire Wilson

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Received 28 September 2001; accepted 8 November 2001

Abstract

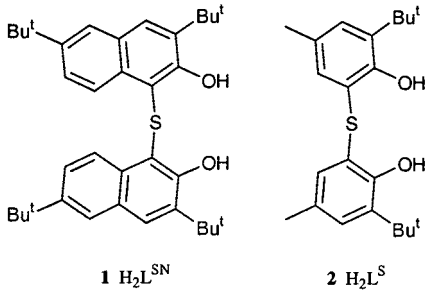
The new thio-binaphthol 2,2′thiobis(3,6-di-*tert*-butylnaphth-2-ol), and a phenolic analogue 2,2′thiobis(6-*tert*-butyl-4-methyl phen-2-ol) react with the Sm(III) aryloxide [$Sm(OC_6H_3Bu^t_2\text{-}2,6)_3$] to give the first f-element complexes supported by S-bridged biphenolate or binaphtholate ancillary ligands, [$Sm\{1,1'\text{-}S(2\text{-}OC_{10}H_4Bu^t_2\text{-}3,6)_2\}(OC_6H_3Bu^t_2\text{-}2,6)]_2$ and [$Sm\{1,1'\text{-}S(2\text{-}OC_6H_2Bu^t\text{-}3\text{-}Me\text{-}5)_2\}(OC_6H_3Bu^t_2\text{-}2,6)]_2$. Symmetric and asymmetric derivatives of both ligands have been prepared by careful tuning of the preparative procedure, the asymmetric naphtholate derivative, and the ligand from which it derives have both been structurally characterised. The asymmetric derivatives are found to be highly selective catalysts for diol desymmetrisation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulfur biphenolate; Sm(III) Lewis acid; Binaphtholate ancillary ligands; Aryloxide; Asymmetric monoacylation; Desymmetrisation

1. Introduction

The continuing development of alternatives to the bis(Cp) ancillary ligand set in lanthanide chemistry constantly reveals new catalysts and unusual small-molecule activation reactivity. As robust, cheap, tuneable, and even potentially recyclable ancillary sets for mediating the reactivity of these electropositive cations, mono-and bidentate alkoxides have become increasingly popular [1].

The replacement of a cyclopentadienyl ligand with the harder, isolobal, monodentate phenolate fragment, for example to form complexes such as $[Cp^*Y(OC_6H_3Bu^t_2\text{-}2,6)H]_2$, [2] can be advantageous in that the harder aryloxide ligand suppresses β-elimination in ethene polymerisation reactions. The incorporation of harder ligands also generates complexes such as $[(Me_3SiH_2C)_2Y(OC_6H_3Bu^t_2\text{-}2,6)(thf)_2]$ [3] that catalyse ε-caprolactone ring-opening polymerisation in addition to ethene polymerisation chemistry. The use of a bidentate ligand to support such reactivities has the advantage of avoiding destructive ligand redistribution reactions, and allows the opportunity to design asymmetry into the ligand set. For example, the lanthanide alkyl *o*-*tert*-butylbiphenolate chelate [$La\{CH(SiMe_3)_2\}\{1,1'\text{-}(2\text{-}OC_6H_2Bu^t_2\text{-}3,5)_2\}$] has a very low energy barrier for the twisting motion that eclipses the two phenol planes and destroys the chirality of the complex, whereas the analogous *o*-triphenylsilylbinaphtholate derivative [$La\{CH(SiMe_3)_2\}\{1,1'\text{-}(2\text{-}OC_{10}H_5SiPh_3\text{-}3)_2\}$-



1 H_2L^{SN} **2** H_2L^S

Fig. 1. 2,2′Thiobis(3,5-*tert*-butyl-2-naphthol), $\mathbf{H_2L^{SN}}$, **1** and 2,2′thiobis(6-*tert*-butyl-4-methylphenol), $\mathbf{H_2L^S}$, **2**.

* Corresponding author. Tel.: +44-115-9513437; fax: +44-115-9513563.

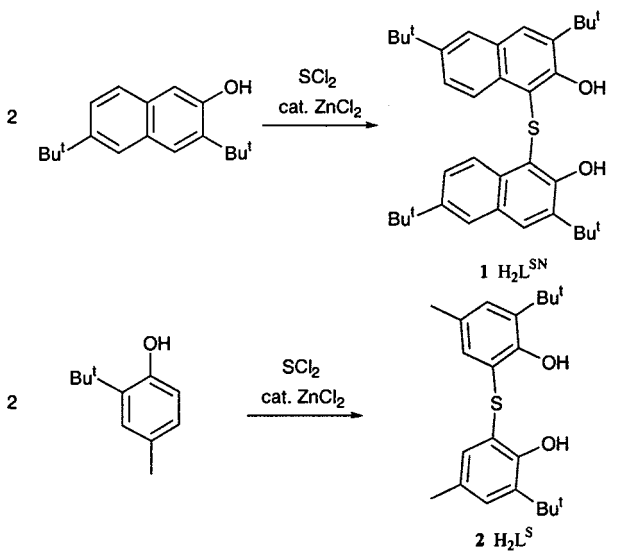
E-mail address: polly.arnold@nott.ac.uk (P.L. Arnold).

PII: S0022-328X(01)01425-5

(OEt_2)] is a rigid C_2-symmetric complex [4]. The latter also undergoes insertion reactions of CO, but no catalytic activity has been reported for these alkyl complexes. Less sterically hindered binol derivatives have more recently been used to access an interesting range of homoleptic, symmetric and asymmetric Lewis acidic catalysts for organic transformations [5].

To date, the potential of the sulfur-bridged biphenolate ligand 2,2′thiobis(6-*tert*-butyl-4-methyl phenol), $\mathbf{H_2L^S}$, Fig. 1, has not been studied as an ancillary ligand set for f-element co-ordination chemistry. This chelating biphenolate has an exemplary record as an auxiliary ligand set in transition metal catalysis-serving to stabilise highly active Ti(IV) polymerisation catalysts, [6] and a copper system that behaves as a functional model for Galactose Oxidase in its catalysis of the aerial oxidation of both primary and secondary alcohols [7].

The ligand $\mathbf{H_2L^S}$ has been described as a 'breathing ligand' in early transition metal chemistry due to the ability of the weakly co-ordinating sulfur to reversibly bind to the metal centre during a reaction. Theoretical studies based on DFT methods suggest that the labilising effect of the electron-rich sulfur atom of a Group 4 olefin polymerisation catalyst not only reduces the energy barrier for ethene binding in the *trans* position, but also lowers the energy barrier for the alkene insertion process [8]. These predictions were borne out when the Group 4 complexes were later synthesised and structurally characterised [6]. In addition, stereoregular polymers were produced when sufficient steric bulk was incorporated at the *ortho* positions of the ligand. This non-innocent, reversible *trans*-labilisation of a substrate in electropositive metal–$\mathbf{L^S}$ complexes is anticipated to lead to the activation/functionalisation of a range of small molecules and new types of Lewis acid catalysts for certain organic transformations. We herein report our synthesis of the first f-element derivative of this type of sulfur-bridged-bisaryloxide ligand; a Sm(III) derivative of the new thio-binaphtholate dianion derived from **1**, and a comparison of its catalytic reactivity with the Sm(III) biphenolate analogue, to our knowledge, the first use of **2** as a ligand in lanthanide co-ordination chemistry.



Scheme 1. Preparation of S-bridged binaphthol and biphenols, $\mathbf{H_2L^{SN}}$ and $\mathbf{H_2L^S}$.

2. Results and discussion

Surprisingly to date there have been no reported lanthanide complexes containing heteroatom-bridged biphenolate or binaphtholate ligands. Our aims in this study were to gain an understanding of the ability of the sulfur donor atom in the ancillary ligand set $\mathbf{L^S}$ and $\mathbf{L^{SN}}$ to influence the reactivity of lanthanide derivatives, the relative rigidity of these ligand sets, and the ability of the lanthanide complexes to function as Lewis acid catalysts. Structural studies show the chelated naphtholate ligand is capable of providing an asymmetric, stereochemically rigid ligand framework for Sm(III). Our preliminary data that show the new Sm complexes catalyse the acylation-desymmetrisation of 1,2-diols.

2.1. Ligand synthesis

The first employment of the ligand $\mathbf{H_2L^S}$ was in 1984 and involved the synthesis of new main-group heterocycles with silicon, germanium and phosphorus [9]. It was noted at this time that both sulfur-bridged biphenol and binaphthols yielded the eight-membered ring containing compounds, but alkylation of the *ortho*-aryl positions to produce sterically encumbered diols was pursued only for the biphenol.

The reagent 2-naphthol is alkylated by *iso*butene in refluxing toluene to give 3,6-di-*tert*-butylnaphth-2-ol in good yield, Scheme 1. Both sulfur-bridged derivatives are easily synthesised in a one pot reaction, using a $ZnCl_2$ Lewis acid catalyst (Scheme 1); the desired products **1** and **2** may be recrystallised from hexanes.

The ligand $\mathbf{H_2L^S}$ has previously been structurally characterised [10]. For comparison, a single crystal of $\mathbf{H_2L^{SN}}$ suitable for a structural determination was grown from a cooled diethyl ether solution, the molecular structure of which is shown in Fig. 2. Notably, the two naphthol rings are eclipsed, with the planes twisted with respect to each other by 88.73(2)°. The hydroxyl protons were located in the Fourier map, each oriented in the plane of, and pointing towards the sulfur atom. The sulfur–$C_{naphthol}$ distances, Table 1, are 1.780(2) and 1.785(2) Å, consistent with non-alkylated structurally characterised S-bridged binaphthol compounds [11]; other distances and angles are also as anticipated.

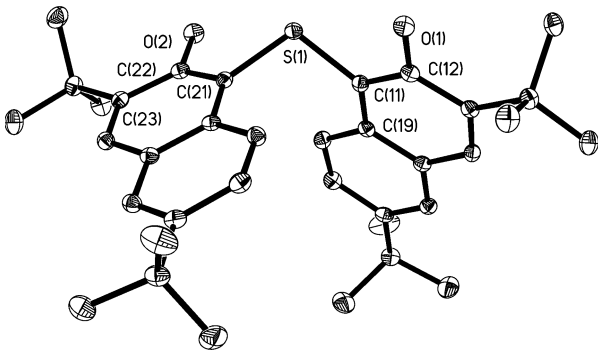


Fig. 2. Ellipsoid plot of the molecular structure of **1**.Et_2O (30% probability). Solvent and H atoms included.

Table 1
Selected distances (Å) and angles (°) for **1**

Bond distances	
S(1)–C(21)	1.780(2)
S(1)–C(11)	1.785(2)
O(1)–C(12)	1.372(2)
O(2)–C(22)	1.376(2)
C(11)–C(12)	1.399(2)
Bond angles	
C(21)–S(1)–C(11)	106.89(9)
C(12)–C(11)–C(19)	120.6(2)
C(12)–C(11)–S(1)	116.11(14)
C(19)–C(11)–S(1)	123.10(14)

2.2. Synthesis of Sm(III) derivatives

The reaction of $\mathbf{H_2L^{SN}}$ with $[Sm(OAr)_3]$, where $OAr = OC_6H_3Bu^t_2$-2,6 in thf or toluene affords

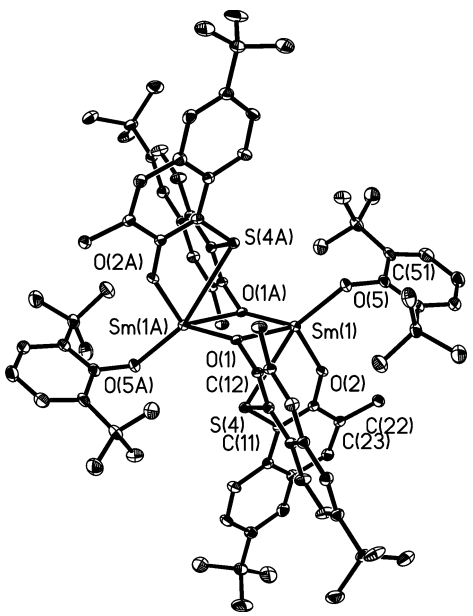
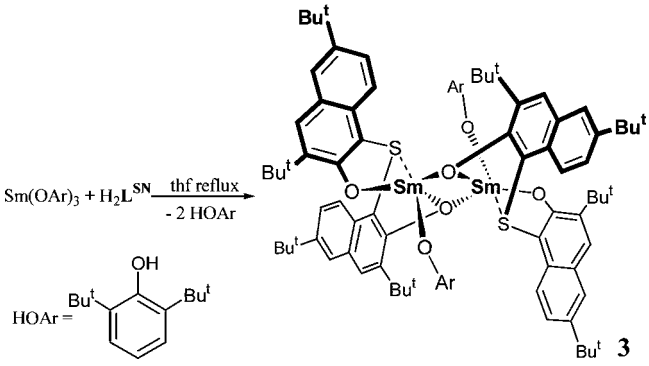


Fig. 3. Ellipsoid plot of the molecular structure of **3** (30% probability). Methyl groups on naphthyl fragments and toluene molecules have been omitted for clarity.

$[Sm\{1,1'\text{-}S(2\text{-}OC_{10}H_4Bu^t_2\text{-}3,6)_2\}(OAr)]_2$ **3**, as an air and moisture-sensitive sunflower-yellow solid, after work up to remove eliminated di-*tert*-butylphenol (Eq. (1)).



(1)

Crude **3** is characterised in solution as an asymmetric dinuclear complex, although samples stubbornly retain one molecule of eliminated phenol rather than thf; this is removed by recrystallisation from hydrocarbon solvents. This dinuclearity is retained in solution at ambient temperature as evidenced by ^{1}H-NMR spectroscopy. Heating a benzene solution of **3** to 350 K in the NMR spectrometer results in a broadening and slight convergence of related resonances of the ligands, but due to partial decomposition in solution at this temperature, the sample was not heated further, so no exchange process can be accessed at low temperatures that render the 'wings' of the naphthyl groups equivalent. It is possible that the decomposition is occurring subsequent to the cleavage of the dimer in the absence of any other additional potential donor ligands.

Single crystals suitable for diffraction were obtained by cooling a toluene solution of **3**; in addition to confirming the asymmetric dinuclearity of **3**, the solid state structure, shown in Fig. 3, has a number of interesting features. Selected distances and angles are reported in Table 2.

The first, rather unusual feature is that one of the naphthyloxide rather than a phenoxide bridges the two metal centres, in accordance with the asymmetry identified by NMR spectroscopy. The twist of 88.79(6)° between the two naphtholate moieties places one ring system between the two metal centres and gives rise to $Sm–O_{naphth}$ distances in the asymmetric core of 2.392(3) and 2.296(3) Å, both at the short end of the range observed to date. This affords an unusually short Sm–Sm′ distance of 3.6084(5) Å. An agostic interaction with the naphthyl *ipso* and *ortho* ring carbons, C11 and C12, is also suggested by the structure. With the sulfur atom co-ordinated to Sm, the $\mathbf{L^{SN}}$ ligand presents a *fac* conformation at Sm. In structurally characterised examples reported to date, the biphenol ligand $\mathbf{H_2L^S}$ has consistently maintained a *fac*- conformation in co-ordi-

Table 2
Selected distances (Å) and angles (°) **3**

Bond distances	
Sm1–O5	2.138(3)
Sm1–O2	2.157(3)
Sm1–O1	2.392(3)
Sm1–O1a	2.296(3)
Sm1–S4	3.1172(11)
Sm1–C11	3.027(4)
Sm1–C12	2.801(5)
Sm1–Sm1a	3.6084(5)
Bond angles	
O5–Sm1–O2	103.17(12)
O5–Sm1–O1	125.08(11)
O2–Sm1–O1	123.98(11)
O5–Sm1–O1a	125.66(11)
O2–Sm1–O1a	95.61(11)
O1a–Sm1–O1	79.38(11)
O5–Sm1–S4	159.67(9)
O2–Sm1–S4	65.18(8)
O1a–Sm1–S4	73.59(7)
O1–Sm1–S4	59.89(7)

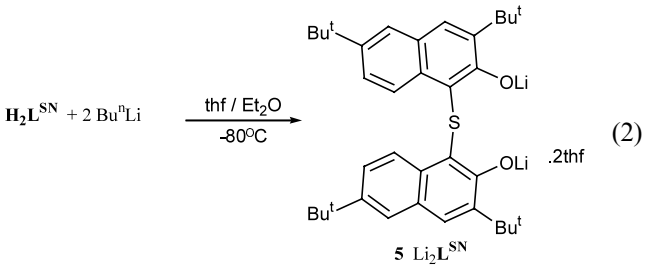
nating to Group 4, 5 and 6 derivatives [12], but adopts a *mer*- conformation around the Cu(II) derivative $[Cu(\mathbf{L^S})]_2Cl_2$ [13]. The terminal phenoxide lies close to a *trans* disposition to the S atom; the Sm–O distance is 2.138(3) Å. Subtraction of the Van der Waals radius for four-co-ordinate Sm^{3+} gives 1.298 Å, which at the long end of the range of values obtained after subtraction of the metal ion radius for structurally characterised Ln^{3+} aryloxide complexes [14]. The Sm–S distance of 3.117(1) Å is long compared with reported lanthanide(III) thioether-substituted cyclopentadienyl, thiophene and crown ligand interactions [15].

The reaction of $\mathbf{H_2L^S}$ with $[Sm(OAr)_3]$ ($OAr = OBu^t_2$-2,6–C_6H_3), at -30 °C in thf affords the first reported f-element $\mathbf{L^S}$ derivative as a thf adduct; $[Sm\{1,1'\text{-}S(2\text{-}OC_6H_2Bu^t\text{-}3\text{-}Me\text{-}5\}(OAr)(thf)]_2$ **4·thf**, is an air and moisture-sensitive bright yellow solid. Interestingly, at ambient temperatures the $\mathbf{L^S}$ adduct **4·thf** is symmetrical in solution, contrary to results observed for the $\mathbf{L^{SN}}$ adduct, **3**. No exchange of solvating thf has been observed in solution. However, purification to remove traces of eliminated phenol from the product (heating in vacuo at 70 °C for 8 h) releases co-ordinated thf as well as residual phenol, to give an asymmetric complex **4**, which is presumably the related thiophenolate-bridged dimer, analogous to **3**, Scheme 2. A range of mass spectrometry and NMR spectroscopy experiments also support this formulation.

We have been unable so far to grow single crystals suitable for X-ray analysis, and without further structural information we cannot rule out the possibility of an η^6-arene interaction in **4**, between each Sm ion and the arene of $\mathbf{L^S}$, as is observed after desolvation of the monomeric $[Ln(C_6H_3\text{-}Ph_2\text{-}2,6)_3]$ and dimeric $[Ln(C_6H_3\text{-}Pr^i_2\text{-}2,6)_3]_2$ aryloxide complexes [16]. However, the chemical shift differences between the two sets of aryl-H resonances (which were originally identical) are small, so the absence of such an electrostatic interaction with one arene is not considered likely.

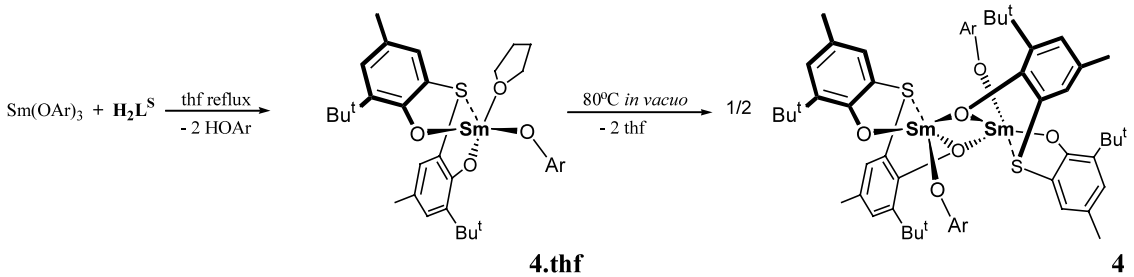
The stabilisation of Group 3 and lanthanide complexes by forming bonding interactions with neutral thioether groups has predominantly been studied for thiophene and thioether-crown ligands. From the measured structural rigidity of the derivatives **3** and **4**, we infer that the bridging sulfur atom interaction in the $\mathbf{L^S}$ and $\mathbf{L^{SN}}$ derivatives must provide a strong electrostatic influence on stabilising the structures.

2.3. Dilithio biphenolate and binaphtholate precursors for Sm(III) L^{SN} and L^S complexes

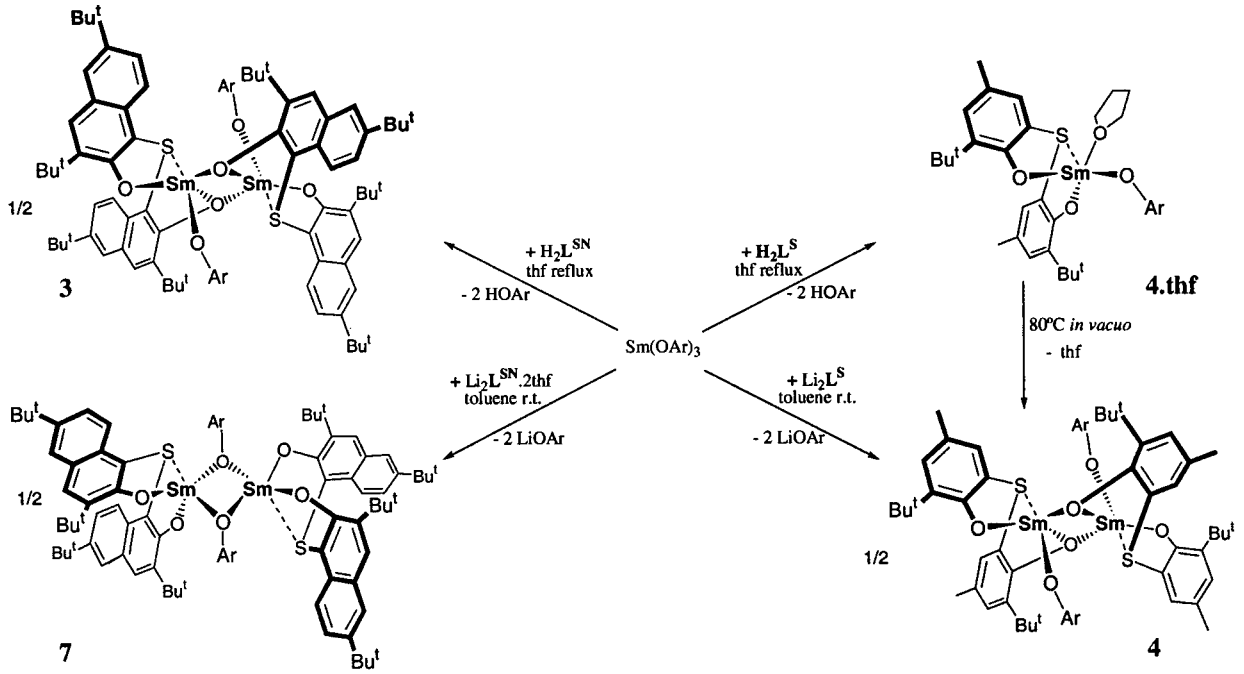


(2)

The elimination of phenolic byproducts from the syntheses of **3** and **4** involves prolonged heating, so we have sought an alternative metathetical route to the $\mathbf{L^S}$ and $\mathbf{L^{SN}}$ derivatives. Okuda et al. have recently reported the in situ preparation of $Li_2\mathbf{L^S}$ in hexane/thf



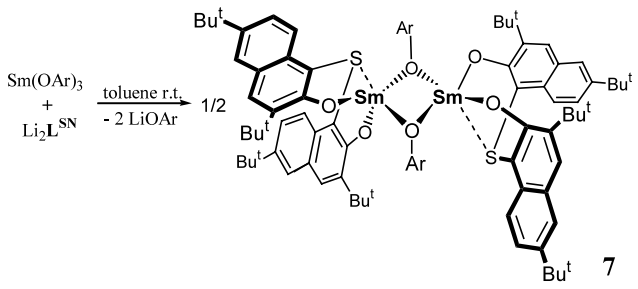
Scheme 2. Synthesis of Sm($\mathbf{L^S}$) derivatives.



Scheme 3. Preparation of symmetric and asymmetric binaphtholate and biphenolate derivatives.

solvent [17]. The analogous conversion of **1** to dilithio salts is outlined in Eq. (2); treatment of **1** with *n*-butyllithium in a thf/diethyl ether mixture affords the dilithio salt $Li_2\mathbf{L}^{SN}$.2thf, **5**, cleanly and in good yield. For our purposes, treatment of **2** with lithium bis(trimethylsilyl)amide in diethyl ether affords unsolvated $Li_2\mathbf{L}^{S}$, **6** in high yield and purity after drying in vacuo for 8 h. The ^{1}H-NMR spectral resonances of the dry product are significantly broadened and no ^{13}C-NMR spectrum could be obtained for this complex. Solubility constraints prevent a thf-free synthesis of $Li_2\mathbf{L}^{SN}$, which retains two moles of co-ordinated thf.

2.4. Alternative syntheses of Sm(III) L^{SN} and L^{S} complexes from metathetical routes



(3)

Treatment of the thf-solvate **5** with $[Sm(OAr)_3]$ in toluene results in the immediate precipitation of eliminated [LiOAr] and the formation of yellow, toluene-soluble complex **7** which is symmetrical, Eq. (3). The complex $[Sm\{1,1'\text{-}S(2\text{-}OC_{10}H_4Bu^t_2\text{-}3,6)_2\}(OAr)]_2$ **7**, unexpectedly contains no co-ordinated thf, even though the reaction solvent is thf and the lithiated reagent incorporates thf. This shows an unexpected difference between the biphenolate and binaphtholate ligands; the syntheses of the derivatives is summarised in Scheme 3. The reaction of base-free $Li_2\mathbf{L}^{S}$, **6**, with $[Sm(OAr)_3]$ also proceeds very cleanly at 20 °C in toluene within a few hours, to give **4** – the unsolvated, asymmetric dinuclear $\mathbf{L}^{S}$ complex which was originally isolated after prolonged heating in the absence of thf. We are unable to isolate the thf solvated, samarium binaphtholate from any of the reactions we have attempted so far. The combination of biphenolate, aryloxide and thf ligands is capable of stabilising the monomeric Sm(III) centre (as **4.thf**), but the analogous naphthyloxide combination is not (**3** and **7** are identified instead). We do not have structural data for **4** that would allow us to identify a stabilising interaction of the S atom. So far we have seen no evidence for any interconversion between **3** and **7**, and so infer a significant rigidity of the twisted binaphtholate conformation in the Sm complexes.

Of the factors that determine the bonding in electropositive metal-aryloxides, the most relevant in a comparison between the $\mathbf{L}^{SN}$ and the $\mathbf{L}^{S}$ systems is probably the π-interaction between the O(2p) orbitals and the aryl ring (MO^+Ph^-) [18]. The relative ability of the aryloxide and naphthyloxide to stabilise an anionic charge on the O atom may explain the inability of simply an additional thf molecule to stabilise a monomeric naphthyloxide derivative.

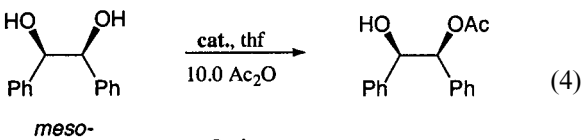
3. Reactivity of 3 and 4 as promoters for selective acylation

To identify whether these ligand sets can stabilise new Sm-based Lewis Acid catalysts, we have studied the ability of **3** and **4** to catalyse the acylation of 1,2-diols, Eq. (4).

The selective protection of chemically similar alcohol groups is a key tool in organic synthetic methodology [19]. While sterically or electronically different hydroxyls may be selectively modified with ease, methods for the mono-functionalisation of similar hydroxyl groups are decidedly fewer in number, although this is a particularly useful derivatisation in large-molecule synthesis. Traditional methods for this are multi-step or time consuming, requiring procedures such as continual extraction methods, heterogeneous or solid supported methods or the selective opening of cyclic 'acetal-like' systems [20]. It has recently been discovered that Lewis acid lanthanide trihalides can promote the reaction with greater efficiency and selectivity than the previously used methods, although to date, we have no information about the mechanism of action, or whether this selectivity can be broadened to encompass 1,3-diol desymmetrisation reactions [21].

Under an atmosphere of dry dinitrogen, a thf solution of *meso*-hydrobenzoin was treated with an excess (10 equivalents) of acetic anhydride and a Sm(III) complex at 10 mol% at 25 °C (Eq. (4)), and the reaction monitored over 24 h.

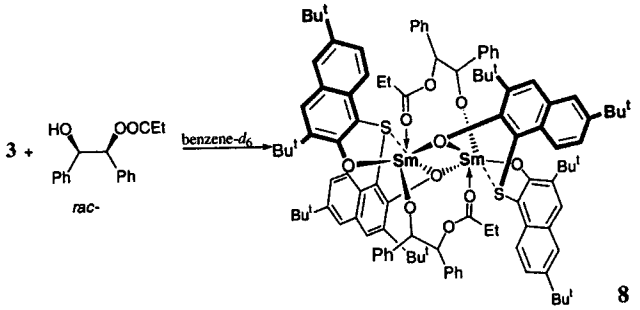
By the end of 24 h, using **3** as a promoter for the reaction resulted in 34% monoesterification of the diol (i.e. the ratio of diol:monoacylated:bisacylated product was 2:1:0). So the complex is a slow but highly selective catalyst for this acylation procedure. By the end of the same time period, using **4** as a promoter resulted in 50% monoesterification of the diol (i.e. the ratio of diol:monoacylated:bisacylated product was 1:1:0). The reactions studied so far have only been allowed to progress for 24 h at room temperature, but it is clear that both are effective, and selective catalysts for the desymmetrisation reaction. By way of comparison, reactions with standards $SmCl_3$ (thionyl chloride/thf dried), and $[Sm(OAr)_3]$, for 24 h the ratio of diol:monoacylated:diacylated product was 0:2:3 and 3:1:0, respectively, i.e. either unselective diacylation or very little conversion.



meso-

cat. = **3**, **4**, $Sm(OAr)_3$ or $SmCl_3$ (4)

The fact that tractable $\mathbf{L}^{SN}$ and $\mathbf{L}^{S}$ complexes of a paramagnetic metal can promote this reaction has prompted an attempt to identify possible intermediates in the catalytic cycle. In an NMR tube fitted with a ptfe valve the binaphtholate **3** was treated with one equivalent of *meso*-hydrobenzoin, in the absence of acylating agent. Within 10 min resonances due to both **3** and the diol have disappeared with only traces of unidentified diamagnetic material remaining. The analogous reaction with the monoacylated product also resulted in the disappearance of any tractable adduct from the NMR spectrum. However, the reaction of **3** with the propylester derivative proceeds over 15 h to afford a stable adduct identifiable by its ^{1}H-NMR spectrum as a paramagnetic Sm derivative **8**, Eq. (5).



(5)

Both terminally co-ordinated phenolate ligands in the dimer have been replaced by propionate, which show strongly paramagnetically shifted H resonances. Although the asymmetric naphtholate framework remains virtually unperturbed, two equivalents of either the *R*- or *S*- form of the ester bind to any one dimer, since two sets of resonances for the ester are observed.

4. Conclusions

The new thio-binaphthol 2,2′thiobis(3,6-di-*tert*-butylnaphth-2-ol), and its phenolic analogue 2,2′thiobis(6-*tert*-butyl-4-methyl phen-2-ol) afford the first f-element Sm(III) complexes supported by S-bridged biphenolate or binaphtholate ancillary ligands, $[Sm\{1,1'\text{-}S(2\text{-}OC_{10}H_4Bu^t_2\text{-}3,6)_2\}(OC_6H_3Bu^t_2\text{-}2,6)]_2$ and $[Sm\{1,1'\text{-}S(2\text{-}OC_6H_2Bu^t\text{-}3\text{-}Me\text{-}5)_2\}(OC_6H_3Bu^t_2\text{-}2,6)]_2$, which exhibit weak interactions with the sulfur atom. The electronic influence of the sulfur atom and the naphthol/phenol groups has been found to influence the stability of the symmetric or asymmetric derivatives of both ligands, as does the preparative procedure. The binaphtholate ligand does not provide sufficient electrostatic stabilisation, in combination with aryloxide and thf ligands, to stabilise a monuclear Sm(III) derivative. However, it provides a highly structurally rigid ancillary ligand for the metal, which can be coordinated in a pseudo-C_{2v} or pseudo-C_2 symmetric fashion. Preliminary results indicate that the asymmetric derivatives are highly found to be highly selective Lewis acid catalysts for diol desymmetrisation, and initial results concerning the interac-

tion of the catalyst and substrate have been obtained for this reaction.

5. Experimental

5.1. General details

All experimental procedures were performed under an atmosphere of dinitrogen or argon, using standard Schlenk techniques or in a glove box under dry nitrogen. Solvents were freshly distilled from the appropriate drying reagent under dinitrogen, and were thoroughly degassed prior to use, diethyl ether from sodium/benzophenone, pentane and toluene from sodium, hexane and benzene-d_6 from potassium, and thf from potassium/benzophenone. ^{1}H-NMR spectra run at 298 K, 300 MHz (400 MHz for experiments in Section 5.3), ^{1}H and ^{13}C referenced versus external TMS, ^{7}Li versus external LiCl at 0.0 ppm. All reagents were obtained from Aldrich, except LiBu^n (Acros), and sulfur dichloride (Acros). 2,2′-Thiobis(6-*tert*-butyl-4-methylphenol) was synthesised according to a literature procedure [22].

5.2. 3,6-$Bu^t_2C_{10}H_5$-2-OH

According to a modification of a literature procedure, [23] 2-naphthol (60 g, 0.42 mole), *p*-TSA (12 g, 0.063 mole), and toluene (200 ml), were added to a 500 ml 3-necked round bottom flask, equipped with stirrer bar, thermometer and gas bubbler. The mixture was heated to 110 °C, and isobutylene gas was bubbled through the solution slowly ($\sim$120 bubbles per min). The reaction was monitored by ^{1}H-NMR. After 12 days, the reaction was quenched by adding $\sim$700 ml water. Toluene was added ($\sim$200 ml) to dissolve the precipitated material, and the layers were separated. The toluene layer was isolated and dried over $MgSO_4$. Subsequent removal of toluene under reduced pressure and recrystallisation from hexane resulted in pure product. The product was isolated as white needles, yield 18% (19.19 g), m.p. 135 °C.

NMR/$CDCl_3$ δ_H 1.41 (s, 9H, 6-Bu^t), 1.52 (s, 9H, 3-Bu^t), 5.00 (s, 1H, O*H*), 6.97 (s, 1H, 1-H), 7.50 (dd, 1H, 7-H, $^3J_{HH}$ 8.63 Hz, $^4J_{HH}$ 1.86 Hz), 7.57 (d, 1H, 8-H, $^3J_{HH}$ 8.63 Hz). 7.70 (s, 2H, 4-H, 5-H). δ_C 153.6 (2-C), 145.6 (1-C), 138.4 (4-C), 131.1 (5-C), 128.4 (8-C), 125.6 (7-C), 124.8 (10-C), 124.4 (9-C), 122.6 (3-C), 110.0 (6-C), 31.2 (3-Bu^t), 29.7 (6-Bu^t). IR (nujol mull) ν(cm^{-1}): 3517 (b), 2945(s), 1261(s), 1018 (m), 8619 (w), 805 (w), 722.18 (w). EIMS: m/z 256 (55% [M]$^+$). Anal. Calc. for $C_{18}H_{24}O$: C, 84.38; H, 9.38. Found: C, 84.76; H, 9.81%.

5.2.1. H_2L^{SN} (1)

To an ethereal solution of 3,6 di-*tert*-butyl-2-naphthol (10 g, 390 mmol, 40 ml) at 0 °C was added 0.04 g $ZnCl_2$ (0.176 mmol). A solution of 1.55 ml (0.195 mmol) sulfur dichloride in 15 ml diethyl ether was added dropwise over a period of 30-min. On completion of addition, the reaction was left stirring for a further 30 min under a slow N_2 sweep to remove evolved HCl, by which time the product had precipitated. The solid was washed at -30 °C with diethyl ether (3 × 20 ml). Pure **2** was isolated as a white powder in 70% yield (7.28 g). M.p. 234–237 °C.

NMR/C_6D_6 δ_H 8.41 (d, 1H, 8-H, $^3J_{HH}$ 8.9 Hz), 7.58 (d, 1H, 5-H, $^4J_{HH}$ 1.89 Hz), 7.63 (s, 1H, 4-H) 7.47 (dd, 1H, 7-H, $^3J_{HH}$ 8.9 Hz, $^4J_{HH}$ 1.89 Hz), 1.51 (s, 9H, 3-Bu^t), 1.19 (s, 9H, 6-Bu^t). δ_C ($CDCl_3$) 155.2 (2-C), 146.4 (1-C), 137.9 (8-C), 131.1 (5-C), 129.1 (4-C), 128.1 (7-C), 125.8 (3-C), 124.1 (10-C), 123.1 (9-C), 110.2 (6-C), 31.3 (3-Bu^t), 29.7 (6-Bu^t). IR (nujol mull) ν(cm^{-1}): 3399 (w), 1170 (w), 1081 (w), 818 (w). EIMS: m/z 540 (82%, [M$^+$]-2H). Anal. Calc. for $C_{36}H_{46}O_2S$ $0.5Et_2O$: C, 78.71; H, 8.86. Found: C, 78.36; H, 8.52%. Crystals suitable for X-ray diffraction were grown by slow cooling of a diethyl ether solution of **1** to -30 °C.

5.2.2. Sm[L^{SN}](OC_6H_3-Bu^t_2-2,6) (3)

To a solution of 0.300g (3.9 mmol) $Sm(OAr)_3$ in 15 ml thf at -30 °C was added dropwise a solution of $H_2\mathbf{L^{SN}}$ 0.213 g (3.9 mmol) in 15 ml thf over a period of 60-min. The solution was allowed to warm to room temperature (r.t.) with stirring. After 24 h, all volatiles were removed under reduced pressure and residual 2,6-di-*tert*-butyl phenol sublimed onto a cold finger yielding a yellow solid. The solid was recrystallised from toluene, yielding pure **3** in 42% yield (147 mg).

NMR/C_6D_6 δ_H 10.87 (d, 1H, 8-H, $^3J_{HH}$ 8.52 Hz), 9.67 (d, 1H, 8-H, $^3J_{HH}$ 7.77 Hz), 9.05 (s,1H, 4-H), 8.75 (s, 1H, 4-H), 8.60 (d, 1H, 5-H, $^3J_{HH}$ 8.97 Hz), 8.14 (d, 1H, 5-H $^3J_{HH}$ 7.41 Hz), 7.44 (d, 1H, 7-H $^3J_{HH}$ 8.97 Hz), 6.03 (d, 1H, 7-H, $^3J_{HH}$ 8.40 Hz), 8.75 (m, 3H OAr), 3.59, 0.18 (s, 9H, 6-Bu^t), 1.73, 1.60 (s, 9H, Bu^t-OAr), -1.49, -4.41 (s, 9H, 3-Bu^t). δ_C 4.0, -3.2 (6-Bu^t), 1.2, 0.8 (Bu^t-OAr), -5.9, -41.8 (3-Bu^t). Only the Bu^t resonances were visible in the ^{13}C-NMR spectrum. EIMS m/z 1588 (100%, [{M–HOAr]$^+$), 1012 (23%, [{M–($C_{10}H_3Bu^t_2$)$_3$–CBu^t]$^+$). Anal. Calc. for $C_{100}H_{130}O_6S_2Sm_2$: C, 67.01; H, 7.26. Found: C, 61.66; H, 7.45%. Repeated determinations give the same results, suggesting metal carbide formation. Crystals suitable for X-ray diffraction were grown by slow cooling of a toluene solution of **3** to -30 °C.

5.2.3. Sm[L^S](OC_6H_3-Bu^t_2-2,6)(thf) (4·thf)

A thf solution of $H_2\mathbf{L^S}$ (47 mg, 0.13 mmol, 10 ml) was added dropwise to a stirring thf solution of

$Sm(OAr)_3$ (100 mg, 0.13 mmol, 10 ml) at −30 °C over 30 min. The solution was then heated to reflux. After 120 h, the solvent was removed under reduced pressure yielding an oily yellow solid **4.thf** in 66% yield (61 mg).

NMR/C_6D_6 δ_H 9.45 (s, 2H, aryl *H*), 8.28 (d, 2H, *m*-OAr $^3J_{HH} = 7.7$ Hz), 7.67 (t, 1H, *p*-OAr $^3J_{HH} = 7.7$ Hz), 7.61 (s, 2H, aryl *H*), 2.69 (s, 6H, CH_3), 2.61 (thf), 1.76 (s, 18H, Bu^t-OAr), 0.91 (thf), 0.26 (s, 18H, Bu^t-L^s). Only the Bu^t and Me resonances were visible in the ^{13}C-NMR spectrum. δ_C 36.4 (s, $C(CH_3)_3$-OAr), 35.4 (s, $C(CH_3)_3$-L^s), 33.0 (s, C(CH_3)$_3$-OAr), 31.9 (s, C(CH_3)$_3$-L^s), 22.6 (s, CH_3).

Coordinated volatiles were removed by sublimation under reduced pressure onto a cold finger, affording a yellow solid **4** in 34% yield (32 mg).

NMR/C_6D_6 δ_H 9.77 (m, 1H, *m*-OAr), 8.78 (t, 1H, *p*-OAr $^3J_{HH} = 7.7$ Hz), 8.61 (s, 1H, aryl *H*), 8.52 (s, 1H, aryl *H*), 8.23 (m, 1H, *m*-OAr), 7.41 (s, 1H, aryl *H*), 6.88 (s, 1H, aryl *H*), 2.71 (s, 3H, CH_3), 1.42 (s, 9H, Bu^t-OAr), 0.22 (s, 9H, Bu^t-OAr), −1.24 (s, 3H, CH_3), −1.66 (s, 9H, Bu^t-L^s), −4.30 (s, 9H, Bu^t-L^s). δ_C 152.9, 138.9, 135.3, 134.7, 133.0, 129.8, 129.6, 128.4, 128.2, 127.9, 127.7, 127.5, 125.4, 125.2, 124.3, 123.9, 118.9, 115.8 (s, aryl C), 36.4, 35.6 (s, CMe_3OAr), 30.9, 30.3 (s, CMe_3Ar), 33.0, 31.9 (s, CMe_3OAr), 28.9, 22.5 (s, CMe_3Ar), 30.0, 20.2 (s, *Me*). FABMS *m*/*z* 1370 (100%, [M–C_3H_3Me]$^+$), 1196 (7%, [M–$C_3H_3C_6H_3Bu^t_2$]$^+$), 1158 (8%, [M–$C_6H_2Bu^t_2Me_2SO$]$^+$). Anal. Calc. for $C_{36}H_{44}O_3SSm$: C, 60.71; H, 6.94. Found: C, 53.88; H, 7.78%.

5.2.4. 2,2′-$Li_2[L^{SN}]$·2thf (**5**)

To a diethyl ether:thf (5:2) solution of $H_2\mathbf{L^{SN}}$ (2.0 g, 3.69 mmol, 35 ml), at −78 °C was added Li^{n}Bu (4.60 ml, 1.6 M in hexane, 7.38 mmol) dropwise over 30 min. The solution was allowed to warm to r.t. with stirring. After 24 h, the product had precipitated from the reaction mixture. The supernatant was decanted off, and the solid washed with three aliquots of 10 ml cold diethyl ether to yield a fine white powder of **5** in 51% yield. M.p. 220 °C (dec.).

NMR/C_6D_6 δ_H 9.3(d, 1H, 8-H ^3J 8.10 Hz), 7.84(s, 1H, 7-H), 7.76 (s, 1H, 5-H), 7.63(s, 1H 4-H), 1.43(s, 9H, 3-Bu^t), 1.31(s, 9H, 6-Bu^t), 3.05(br, 4H, thf), 0.91(br, 4H, thf), no measurable coupling constants. δ_C 142.4 (2-C), 135.6 (1-C), 124.4 (m, br, 3-C to 10-C), 67.9 (thf) 35.6 (thf), 31.4 (3-Bu^t), 30.4 (6-Bu^t). δ_{Li} 3 (br s). Addition of one drop of distilled water regenerated the ^{1}H-NMR spectrum of $H_2\mathbf{L^{SN}}$. ESMS 438 (100%, [M–2Bu^{t}H]$^+$, 397 (5%, [M–$C_8H_4Bu^t$]$^+$. Anal. Calc. for $C_{36}H_{44}O_2SLi_2$·2thf: C, 74.98; H, 7.99. Found: C, 73.35; H, 8.25%.

5.2.5. 2,2′-$Li_2[L^S]$·xEt_2O (x = 0–2) (**6**)

A solution of $LiN(SiMe_3)_2$ in diethyl ether (2.33 g, 11.2 mmol, 10 ml) was added dropwise to a stirred solution of H_2L^s in diethyl ether (2.0 g, 5.6 mmol, 10 ml), causing the formation of a precipitate. The suspension was allowed to warm to r.t. with stirring over 12 h. The precipitated solid was recrystallised from diethyl ether to yield **6** ($x = 2$) as a white powder in 60% (1.2 g non-optimised yield). Prolonged drying in vacuo reduces *x* to 0.09. Addition of one drop of distilled water regenerated the ^{1}H-NMR spectrum of $H_2\mathbf{L^S}$.

NMR/C_6D_6 δ_H (thf adduct) 7.02 (d, $J = 6.8$ Hz, 4H, aryl *H*), 1.97 (s, 6H, methyl CH_3), 1.47 (s, 18H, C(CH_3)$_3$). δ_{Li} 2.40 (s). δ_H (diethyl ether adduct) 7.59 (s, br, 4H, aryl *H*), 2.10 (s, br, 6H, methyl CH_3), 1.28 (s, br, 18H, C(CH_3)$_3$). δ_{Li} 1.82 (br s). δ_C 31.1 (s, C(CH_3)$_3$), 20.7 (s, CH_3). Aryl H were broadened to baseline in non-coordinating NMR solvents, precluding assignment. ESMS (MeOH solution) 466 (18%, [M.3MeOH]$^+$), 241 (9%, [M–Bu$^t_2$Me]$^+$). Anal. Calc. for $C_{22}H_{28}O_2SLi_2$: C, 71.34; H, 7.62. Found: C, 71.98; H, 8.10%.

5.2.6. Reaction of Li_2L^S and $Sm(OAr)_3$ to give $[Sm[L^S](2,6\text{-}Bu^t_2\text{-}OC_6H_3)]_2$ (**4**)

A toluene solution of $Li_2\mathbf{L^S}$ (75 mg, 0.20 mmol, 10 ml) was added dropwise to a stirring toluene solution of $Sm(OAr)_3$ (155 mg, 0.20 mmol, 10 ml) at −30 °C over 30 min. The solution was allowed to warm to r.t. with stirring. After 24 h, the solvent was removed under reduced pressure and the resultant solid recrystallised from a hexane–toluene mixture (4:1), affording a yellow solid **4** in 44% yield (64 mg).

5.2.7. Reaction of Li_2L^{SN} and $Sm(OAr)_3$ to give symmetrical $[Sm[L^{SN}](2,6\text{-}Bu^t_2\text{-}OC_6H_3)]_2$ (**7**)

A toluene solution of $Li_2\mathbf{L^{SN}}$ (456 mg, 0.65 mmol, 15 ml) was added dropwise to a stirring toluene solution of $Sm(OAr)_3$ 500 mg, 0.65 mmol, 15 ml) at −30 °C over 30 min. The solution was allowed to warm to r.t. with stirring. After 24 h, the solvent was removed under reduced pressure and the resultant solid recrystallised from toluene, affording a yellow solid **7** in 20% yield (230 mg).

NMR/C_6D_6 δ_H 9.57 (d, 1H, 8-H, $^3J_{HH}$ 9 Hz), 7.77 (dd, 7-H $^3J_{HH}$ 9Hz, $^4J_{HH}$ 1.9 Hz), 7.48 (d, 1H, 5-H, $^4J_{HH}$ 1.9 Hz), 7.27 (s, 1H, 4-H), 6.87, (m, 3H OAr), 1.35 (s, 9H, 6-Bu^t), 1.10 (s, 9H 3-Bu^t), 1.73 (s, 9H, Bu^t-OAr).

5.3. 1,2-Diol desymmetrisation catalysis

To a stirring solution of [catalyst] (20 mg, 10 mol%) (where $x = SmCl_3$, $Sm(OAr)_3$, Sm[$\mathbf{L^{SN}}$](2,6-Bu$^t_2$-OC_6H_3) **3**, Sm[$\mathbf{L^S}$](2,6-Bu$^t_2$-OC_6H_3) **4**) and *meso*-hydrobenzoin in thf (2.4 ml) was added acetic anhydride (ten equivalents). The reaction was monitored by TLC (1:1 diethyl ether:hexane). After 24 h, the reaction was diluted with ethyl acetate (25 ml), and washed successively with saturated $NaHCO_3$ (2 × 20 ml) and brine (20 ml). The

organics were dried ($MgSO_4$) and the solvent evaporated to give the crude product, which was purified by recrystallisation from ethyl acetate/hexane. The spectroscopic data for the products were identical to that previously reported in the literature [24].

5.4. NMR tube reactions

5.4.1. Reaction of **3** with meso-hydrobenzoin

A Youngs ptfe tap equipped NMR tube was charged with 5.0 mg (1.68 μmol) **3** in d_6-benzene and one equivalent of *meso*-hydrobenzoin in d_6-benzene (1.68 μmol, 0.4 mg) resulted in an immediate colour change from yellow to pale brown. The ^{1}H-NMR spectrum showed no NMR-active species other than trace diamagnetic impurities.

5.4.2. Reaction of 3 with meso-(2-acetoxy-1,2-biphenylethanol)

A Young's ptfe tap equipped NMR tube was charged with a d_6-benzene solution of **3** (5.0 mg, 1.68 μmol), and *meso*-(2-acetoxy-1,2-biphenylethanol) (*meso*-hydrobenzoin) (1.0 mg, 3.36 μmol). The yellow solution became pale brown over 15 min, and the ^{1}H-NMR spectrum showed no NMR-active species other than trace diamagnetic impurities.

5.4.3. Reaction of **3** with rac-hydrobenzoin-2-propanoyl ester

In a Youngs ptfe tap equipped NMR tube, two equivalents of *meso*-hydrobenzoin-2-propanoyl ester (1.0 mg, 3.36 μmol) in d_6-benzene were added to a d_6-benzene solution of **3** (5.0 mg, 1.68 μmol). No colour change from pale yellow was observed. The ^{1}H-NMR spectrum of the reaction mixture 15 h after addition shows no residual starting materials, large free ArOH peaks and no paramagnetically shifted OAr moieties.

NMR/C_6D_6 δ_H 8.96 (d, 1H, 8-H, $^3J_{HH}$ 10.56 Hz), 8.52 (d, 1H, 8-H, $^3J_{HH}$ 8.76 Hz), 8.37, 7.98 (s, 1H, 5-H), 8.34, 7.88 (s, 1H, 4-H), 7.53 (d, 1H, 7-H, $^3J_{HH}$ 6.9 Hz), 7.29 (d, 1H, 7-H, $^3J_{HH}$ 8.37 Hz), 6.97, 6.24 (m, 5H, Ph), 3.89, 3.66 (s, 3H, CH_3), 1.55, 1.25 (s, 9H, 3-Bu^t), 1.22, 0.88 (s, 9-H, 6-Bu^t), 1.59, 0.68, −2.02, −4.57 (s, 1H, CH), −2.83, −6.21 (s, 2H, CH_2).

Table 3
Crystallographic data for $[H_2L^{SN}]$ (**1**) and $[Sm(L^{SN})(Bu^t_2OC_6H_3)]_2$ (**3**)

	$[H_2L^{SN}]$	$[Sm(L^{SN})(Bu^t_2OC_6H_3)]_2$
Empirical formula	$C_{40}H_{56}O_3S$	$C_{71}H_{89}O_3SSm$
Formula weight (g mol^{-1})	616.91	1172.83
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$
Unit cell dimensions		
a (Å)	11.542(2)	18.2022(11)
b (Å)	11.899(2)	12.7397(8)
c (Å)	13.571(2)	27.862(2)
α (°)	88.106(2)	
β (°)	87.369(2)	100.8860(10)
γ (°)	78.311(2)	90
V (Å^3)	1822.8(5)	6344.7(7)
Z	2	4
Absorption coefficient (mm^{-1})	0.123	1.003
Crystal size (mm), colour	0.26 × 0.14 × 0.12, colourless	0.13 × 0.10 × 0.08, yellow
Habit	Block	Hexagonal prism
Reflections collected, unique	15 799, 7977 [R_{int} = 0.086]	14 957, 8584 [R_{int} = 0.069]
Reflections observed ($>2\sigma$)	4633	8584
Absolute correlation, T_{min}, T_{max}	None	Multi-scan, 0.869, 0.928
Number of parameters	399	592
Completeness to 2θ = 55°/(%)	95.3	98.7
Final R indices [$I\sigma 2(I)$]c	R_1 = 0.0501, wR_2 = 0.1055	R_1 = 0.0500, wR_2 = 0.1071
R indices (all data)	R_1 = 0.0952, wR_2 = 0.1196	R_1 = 0.1062, wR_2 = 0.1211
Residual extrema (e Å^{-3})	0.354 and −0.240	1.228 and −0.653

5.5. Crystallographic data

X-ray data, see Table 3, were collected using Mo–K_α radiation (λ = 0.71073 Å) on a Bruker SMART1000 CCD area detector diffractometer using ω scans. Structure solution and refinement was carried out using the SHELX suite of programs [25].

6. Supplementary material

Full X-ray crystallographic data and atomic co-ordinates for the ligand **1** and the Sm complex **3**. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 171416 for compound **1** and no. 171417 for compound **3**. Copies of this information may be obtained freeof charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank Dr Paul A. Clarke for help with the catalysis testing and for useful discussions, Dr Ali Abdul Sada for the EIMS data, and the EPSRC (fellowship for P.L.A., studentship for L.S.N. and J.J.H.) and the Royal Society for funding.

References

[1] Reviews: (a) F.T. Edelmann, Angew. Chem. Int. Ed. Engl. 34 (1995) 2466;
(b) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428;
(c) W.J. Evans, New J. Chem. 19 (1995) 525;
(d) C.E. Daitch, P.D. Hampton, E.N. Duesler, T.M. Alam, Am. Chem. Soc. J. 118 (1996) 7769;
(e) G.B. Deacon, P.E. Fanwick, A. Gitlits, I.P. Rothwell, B.W. Skelton, A.H. White, Eur. J. Inorg. Chem. (2001) 1505;
(f) R. Duchateau, T. Tuinstra, E.A.C. Brussee, A. Meetsma, P.T. Van Duijnen, J.H. Teuben, Organometallics 16 (1997) 3511;
(g) L. Lee, D.J. Berg, F.W. Einstein, R.J. Batchelor, Organometallics 16 (1988) 1819;
(h) H.A. Stecher, A. Sen, A.L. Rheingold, Inorg. Chem. 27 (1988) 1130;
(i) D.L. Clark, J.C. Gordon, J.C. Huffman, J.G. Watkin, B.D. Zwick, Organometallics 13 (1994) 4266;
(j) Z.M. Hou, Y.G. Zhang, T. Yoshimura, Y. Wakatsuki, Organometallics 16 (1997) 2963;
(k) W.J. Evans, M.A. Greci, M.A. Johnston, J.W. Ziller, Chem. Eur. J. 5 (1999) 3482;
(l) Z.M. Hou, Y.G. Zhang, H. Tezuka, P. Xie, O. Tardif, T. Koizumi, H. Yamazaki, Y. Wakatsuki, Am. Chem. Soc. J. 122 (2000) 10533.

[2] (a) C.J. Schaverien, J.H.G. Frijns, H.J. Heeres, J.R. Van den Hende, J.H. Teuben, A.L. Spek, Chem. Commun. (1991) 642;
(b) C.J. Schaverien, Chem. Commun. (1992) 11.

[3] W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, J. Organomet. Chem. 569 (1998) 89.

[4] C.J. Schaverien, N. Meijboom, A.G. Orpen, Chem. Commun. (1992) 124.

[5] (a) N. Yoshikawa, J.M.A. Yamada, J. Das, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 121 (1999) 4168;
(b) V.K. Aggarwal, A. Mereu, G.J. Tarver, R. McCague, J. Org. Chem. 63 (1998) 7183;
(c) H.C. Aspinall, J.L.M. Dwyer, N. Greeves, A. Steiner, Organometallics 18 (1999) 1366;
(d) H.C. Aspinall, J.F. Bickley, J.L.M. Dwyer, N. Greeves, R.V. Kelly, A. Steiner, Organometallics 19 (2000) 5416;
(e) H. Ishitani, S. Kobayashi, Tetrahedron. Lett. 37 (1996) 7357;
(f) H. Kodama, J. Ito, K. Hori, T. Ohta, I. Furukawa, J. Organomet. Chem. 603 (2000) 6.

[6] (a) J. Okuda, E. Masoud, Macromol. Chem. Phys. 199 (1998) 543;
(b) A. Van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.

[7] (a) M. Hess, K. Wieghardt, P. Chaudhuri, US Patent 6153779;
(b) H.-J. Krueger, Angew. Chem. Int. Ed. 38 (1999) 627;
(c) P. Chaudhuri, M. Hess, J. Muller, K. Hildenbrand, E. Bill, T. Weyhermuller, K. Wieghardt, J. Am. Chem. Soc. 121 (1999) 9599;
(d) P. Chaudhuri, M. Hess, T. Weyhermuller, K. Wieghardt, Angew. Chem. Int. Ed. 38 (1999) 1095.

[8] R.D.J. Froese, D.G. Musaev, K. Morokuma, Organometallics 18 (1999) 373.

[9] S.D. Pastor, J.D. Spivack, L.P. Steinhenbel, J. Heterocycl. Chem. 21 (1984) 1285.

[10] A. Chetkina, V.E. Zavodnik, V.K. Bel'skii, I.G. Arzamanova, M.I. Naiman, Y.A. Gurvich, Zh. Strukt. Khim. 25 (1984) 114.

[11] (a) M. Krishnaiah, K.D. Berlin, Heteroat. Chem. 6 (1995) 485;
(b) O.N. Kataeva, I.A. Litvinov, V.A. Naumov, I.V. Anonimova, J. Mol. Struct. 344 (1996) 95;
(c) R.M.L. Mercado, A. Chandrasekaran, R.O. Day, R.R. Holmes, Organometallics 18 (1999) 906.

[12] (a) S. Fokken, T.P. Spaniol, H.C. Kang, W. Massa, J. Okuda, Organometallics 15 (1996) 5069;
(b) L. Porri, A. Ripa, P. Colombo, E. Miano, S. Capelli, S.V. Meille, J. Organomet. Chem. 514 (1996) 213;
(c) C.R. Cornman, K.M. Keiser-Bush, J.W. Kampf, Inorg. Chem. 38 (1999) 4303;
(d) Y. Nakayama, H. Saito, N. Ueyama, A. Nakamura, Organometallics 18 (1999) 3149.

[13] P. Chaudhuri, M. Hess, U. Florke, K. Wieghardt, Angew. Chem. Int. Ed. 37 (1998) 2217.

[14] Range calculated = 1.24–1.31 Å. (a) P.L. Arnold, A.J. Blake, S.N. Hall, B.D. Ward, C. Wilson, J. Chem. Soc. Dalton Trans. (2001) 488;
(b) G.B. Deacon, P.E. Fanwick, A. Gitlits, I.P. Rothwell, B.W. Skelton, A.H. White, Eur. J. Inorg. Chem. (2001) 1505;
(c) D.R. Click, B.L. Scott, J.G. Watkin, Chem. Crystallogr. J. 29 (1999) 921;
(d) Y.M. Yao, Q. Shen, K.B. Yu, Acta Crystallogr. Sect. C, Cryst. Struct. Commun. 56 (2000) 1330;
(e) M. Yousaf, Q.C. Liu, J.L. Huang, Y.L. Qian, A.S.C. Chan, Inorg. Chem. Commun. 3 (2000) 105;
(f) R.J. Butcher, D.L. Clark, J.C. Gordon, J.G. Watkin, Organomet. Chem. J. 577 (1999) 228;
(g) Z. Hou, Y. Zhang, T. Yoshimura, Y. Wakatsuki, Organometallics 16 (1997) 2963;
(h) Z.M. Hou, A. Fujita, T. Yoshimura, A. Jesorka, Y.G. Zhang, H. Yamazaki, Y. Wakatsuki, Inorg. Chem. 35 (1996) 7190;
(i) D.L. Clark, J.C. Gordon, J.G. Watkin, J.C. Huffman, B.D. Zwick, Polyhedron 15 (1996) 2279;
(j) G.H. Qi, Y.G. Lin, J.Y. Hu, Q. Shen, Polyhedron 14 (1995) 413;
(k) D.M. Barnhart, D.L. Clark, J.C. Gordon, J.C. Huffman, R.L. Vincent, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 3487;
(l) D.L. Clark, J.C. Gordon, J.C. Huffman, R.L. Vincenthollis, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 5903;
(m) P.B. Hitchcock, M.F. Lappert, A. Singh, Chem. Commun. (1983) 1499;
(n) P.B. Hitchcock, M.F. Lappert, R.G. Smith, Inorg. Chim. Acta 139 (1987) 183;
(o) W.J. Evans, M.A. Johnston, M.A. Greci, J.W. Ziller, Polyhedron 20 (2001) 277.

[15] (a) M. Geissinger, J. Magull, Z. Anorg. Allg. Chem. 623 (1997) 755;
(b) H.J. Heeres, A. Meetsma, J.H. Teuben, J. Organomet. Chem. 414 (1991) 351;
(c) H. Schumann, K. Herrmann, J. Demtschuk, S.H. Muhle, Z. Anorg. Allg. Chem. 625 (1999) 1107.

[16] (a) G.B. Deacon, S. Nickel, P. MacKinnon, E.R.T. Tiekink, Austr. J. Chem. 43 (1990) 1245;
(b) D.M. Barnhart, D.L. Clark, J.C. Gordon, J.C. Huffman, R.L. Vincent, J.D. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 3487.

[17] F. Amor, S. Fokken, T. Kleinhenn, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 621 (2001) 3.

[18] W.A. Howard, T.M. Trnka, G. Parkin, Inorg. Chem. 34 (1995) 5900.

[19] (a) H. Fujioka, Y. Nagatomi, N. Kotoku, H. Kitagawa, Y. Kita, Tetrahedron 56 (2000) 10141;
(b) N. Maezaki, M. Soejima, M. Takeda, A. Sakamoto, T. Tanaka, C. Iwata, Chem. Commun. (1994) 1345;
(c) N. Maezaki, M. Murakami, M. Soejima, T. Tanaka, T. Imanishi, C. Iwata, Chem. Pharm. Bull. 44 (1996) 1146.

[20] (a) J.H. Babler, M.J. Coghlan, Tetrahedron Lett. 20 (1979) 1971;
(b) T. Nishiguchi, H.J. Taya, Am. Chem. Soc. 111 (1989) 9102;

(c) H. Ogawa, M. Amano, T. Chihara, Chem. Commun. (1998) 495;
(d) M. Oikawa, A. Wada, F. Okazaki, S. Kusumoto, J. Org. Chem. 61 (1996) 4469;
(e) P.C. Zhu, J. Lin, C.U. Pittman Jr., J. Org. Chem. 60 (1995) 5729;
(f) N. Maezaki, M. Soejima, M. Takeda, A. Sakamoto, T. Tanaka, C. Iwata, Chem. Commun. (1994) 1345;
(g) G. Egri, E. BaitzGacs, L. Poppe, Tetrahedron: Asymmetry 7 (1996) 1437;
(h) K.F. Hsiao, F.L. Yang, S.H. Wu, K.T. Wang, Biotechnol. Lett. 18 (1996) 1277;
(i) M. Kinugasa, T. Harada, A. Oku, Tetrahedron Lett. 39 (1998) 4529;
(j) H. Fujioka, Y. Nagatomi, N. Kotoku, H. Kitagawa, Y. Kita, Tetrahedron 56 (2000) 10141.

[21] (a) R.A. Holton, Z. Zhang, P.A. Clarke, H. Nadizadeh, D.J. Procter, Tetrahedron Lett. 39 (1998) 2993;
(b) P.A. Clarke, R.A. Holton, N.E. Kayaleh, Tetrahedron Lett. 41 (2000) 2687.

[22] S.D. Pastor, J.D. Spivack, L.P. Steinheubel, J. Heterocycl. Chem. 49 (1984) 4302.

[23] D.W. Chasar, J. Org. Chem. 49 (1984) 4302.

[24] P.C. Zhu, J. Lin, C.U. Pittman, J. Org. Chem. 60 (1995) 5729.

[25] (a) Bruker, SHELXTL 5.10. Bruker AXS Inc., Madison, Wisconsin, USA, 1997. G.M. Sheldrick Acta Crystallogr Sect. A 46 (1990) 467;
(b) G.M. Sheldrick, SHELXL97, University of Göttingen, Germany 1997.