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Sulfur-bridged phenoxide and naphthyloxide-based ligands for lanthanide chemistry and catalysis

Louise S. Natrajan, Jonathan J. Hall, Alexander J. Blake, Claire Wilson, and Polly L. Arnold*

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

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Abstract

The development of some new lanthanide chemistry of aryloxide-based ligands is presented. The use of chelating, dianionic aryloxide ligand sets, such as sterically encumbered binolates, to allow a degree of geometrical control over the reaction chemistry of these large metal cations, is reviewed. We show how the development of potentially tridentate, dianionic, sulfur-bridged biphenolate and binaphtholate [OSO] ligands has allowed us to make new *Ln*(III) aryloxide complexes such as [Sm{1,1′-S(2-$OC_6H_2Bu^t$-3,-Me-5)$_2$}($OC_6H_3Bu^t_2$-2,6)(THF)] and [Sm{1,1′-S(2-$OC_{10}H_4Bu^t_2$-3,6)$_2$}($OC_6H_3Bu^t_2$-2,6)(THF)]. Unusually, both symmetric and asymmetric derivatives of the [OSO] ligands may be prepared; reasons for this observation are suggested. Reactivity studies of these Sm(III) derivatives have shown them to be selective Lewis acid catalysts for the one-step monoacylation of 1,2-diols. Oxidation products of the sulfur-bridged binaphtholate ligand have been crystallographically characterized.

Keywords: Samarium; Lanthanide; Aryloxide; Naphthyloxide; Sulfur hemilabile biphenolate catalysis; Desymmetrization; Acylation; Phenoxide

1. Introduction

Following the synthesis of the first homoleptic lanthanide aryloxide complexes 20 years ago, one of the major themes in this area has been the development of aryloxide-based ancillary ligands to support reactive f-element centers. In recent decades, phenolates have taken on a variety of roles as ligands for the stabilization of *f*-element coordination complexes [1]. The *Ln*–OAr bond is thermodynamically strong but unlike cyclopentadienyl anions, aryloxide ligands do not impart a high level of kinetic stability on a complex unless large *ortho*-substituents such as *tert*-butyl groups are incorporated [2]. The first isolated *F*-element aryloxide derivatives were homoleptic, trivalent tris(aryloxide) complexes, derived from phenolates incorporating bulky *ortho*-substituents; the complexes Ln(OC_6H_2–Bu^t_2Me)$_3$ (Ln = Sc, Y **1**, Fig. 1, La, Pr, Nd, Dy, Ho, Er, and Yb) [3] are all hydrocarbon-soluble, air-sensitive, high-melting, crystalline solids. Other homoleptic complexes reported since are Ln(OC_6H_3–Bu^t_2)$_3$ (*Ln* = Y and Ce) [4] and Ln(OC_6H_3–R_2)$_3$ (*R* = Me, Ph, Pr^i, *Ln* = Ce, Sc, Sm, and Yb) [5]. Unless specified otherwise, the arene substituents in the complexes described in this paper are in the 2, 6 or 2, 6, and 4 positions.

The complexes may be made via reactions such as the direct treatment of activated metal (often with trace Hg^{2+} added) with a phenol in liquid ammonia, benzophenone or *iso*-propanol, group transfer from pentafluorophenyl-lanthanide adducts formed in situ, protonolysis of a coordinated amide or alkyl, or metathesis of a trihalide with a Li, Na or K aryloxide [6]. The last method has also been used to make mixed halide–aryloxide complexes [7]. The solvent-free homoleptic adducts are often those most readily isolated due to the use of sublimation as a purification technique. Mononuclear complexes of aryloxides with smaller *ortho*-arene substituents must be isolated as Lewis base adducts [8], and in the absence of coordinated solvent form O-bridged dimers and clusters [9]. Two interesting structural forms have been identified which invoke metal–arene interactions for additional electrostatic stabilization of the electropositive metal center;

*Corresponding author. Fax: +44-115-951-3563.
E-mail address: polly.arnold@nottingham.ac.uk (P.L. Arnold).

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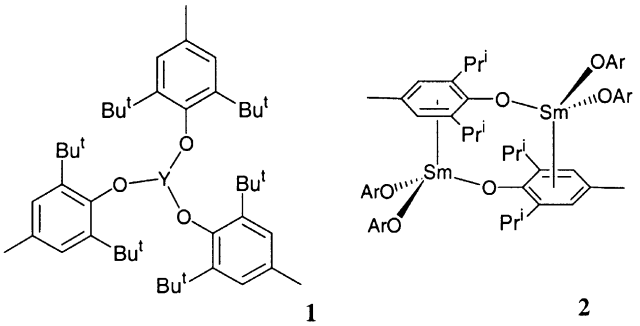


Fig. 1.

these are exemplified by the dinuclear complex $[Sm(OC_6H_3–Pr^i_2)_3]_2$ **2**, Fig. 1, and the mononuclear $Nd(OC_6H_3–Ph_2)_3$ in which one of the *ortho*-arene groups binds in an η^6-conformation to the metal [10].

Incorporation of Group 1 aryloxide precursors can also give 'ate' complexes such as $K[Sm(OC_6H_2–Bu^t_2Me)_3(THF)]$ and $K[Ln(OC_6H_3–Pr^i_2)_4]$ (*Ln* = Er, La) [11]. Both homoleptic and solvated aryloxides of the divalent lanthanides are also readily prepared, including the aryloxide bridged $[Yb(OC_6H_2–Bu^t_2Me)_2]_2$ [12], $Yb(OC_6H_2–Bu^t_2Me)_2(THF)_3$ and $Yb(OC_6H_2–Bu^t_2Me)_2(THF)_2$ [13], $Sm(OC_6H_2–Bu^t_2Me)_2(THF)_3$ [14], $Eu(OC_6H_3–Bu^t_2)_2(MeCN)_4$ and $Eu(OC_6H_2–Bu^t_2Me)_2(Et_2O)_2$ [13,15]. Divalent Tm, Nd, and Dy adducts of this class of ligands have yet to be reported.

The tris(aryloxide) complexes are now commonly used as halide-free starting materials for synthetic *f*-element chemistry, and the *tert*-butyl substituted solvent-free $Ln(OAr)_3$ species are volatile and make excellent precursors for ceramic materials [16]. The complex $Sm(OC_6H_2–Bu^t_2Me)_3$ is a good Lewis acid catalyst for the Tischenko reaction [17], whilst divalent $Sm(OC_6H_2–Bu^t_2Me)_2(THF)_3$ shows extremely high activity as an initiator for the ring-opening polymerization of both ε-caprolactone and δ-valerolactone, producing polyesters with molecular weights as high as 600,000 and narrow molecular weight distributions (<1.65). Although the complex does not polymerize γ-butyrolactone alone, it can copolymerize this monomer with ε-caprolactone [18].

Continued efforts to find alternative ancillary ligand sets for Group 3 and *f*-element alkene polymerization catalysts have yielded mixed alkyl/aryloxide complexes such as $YCp^*(CH\{SiMe_3\}_2)(OC_6H_3–Bu^t_2)$ ($Cp^* = [\eta–C_5Me_5]$), $YCp^*(OC_6H_3–Bu^t_2)_2$, and $Yb(C_5H_4Me)(OC_6H_3–Bu^t_2)_2(THF)$, $SmCp^*_2(OC_6H_3–Bu^t_2)_2$, $[Li(THF)_4][Lu(CH_2SiMe_3)_2(OC_6H_3–Bu^t_2)_2]$, and $NdCp_2(OC_6H_3–Ph_2)(THF)_2$ [19]. The complex $Y(CH_2SiMe_3)(OC_6H_3–Bu^t_2)_2(THF)_2$ polymerizes both ethene and ε-caprolactone, although the related 'ate' complexes with incorporated LiCl – $[Li(THF)_3]_2[Y(CH_2SiMe_3)_2(OC_6H_3–Bu^t_2)_2(THF)_2]Cl$ and $[Li(THF)_4][Lu(CH_2SiMe_3)_2(OC_6H_3–Bu^t_2)_2]$ only polymerize ε-caprolactone [20].

Notably, the replacement of one Cp^* ligand in $SmCp^*_2(THF)_2$ with a monodentate OAr^- ligand gives a unique catalytic system that can polymerize styrene and ethene separately, or into block styrene–ethene copolymers [21]. Thermodynamic arguments suggest that the incorporation of a hard aryloxide in an organolanthanide alkene polymerization catalyst should suppress β-elimination reactions; the complex $[YCp^*(OC_6H_3–Bu^t_2)(\mu\text{-}H)]_2$ is a single component catalyst for the formation of isotactic poly(1-hexene) which also cyclopolymerizes 1,5-hexadiene to poly(methylene-1,3-cyclopentane) [22]. Derivatives of soluble silsesquioxane-based polysilanolate ligands have also been isolated, although no catalytic chemistry has yet been reported: these include functionalized adducts of *f*-elements coordinated to aryloxide in $Sm(OC_6H_3Bu^t_2\text{-}2,6)\{(c\text{-}C_5H_9)_7Si_7O_9(O)(OLi)(OSiMe_2Bu^t)\}_2$ [23], cyclopentadienyl in $[Li(THF)]SmCp^*_2[Cy_7Si_8O_{12}O]_2$ [24], and chloride ligands in $LaCl(THF)[Cy_7Si_7O_{11}(OSiMe_3)]$ [25].

In an extension of this work on monoanionic systems, the exploration of rigid, dianionic biphenolate and binaphtholate ligands as potential ancillary ligand sets for stereochemical control in α-olefin polymerization has now begun [26].

Metal alkyl derivatives of *ortho*-trimethylsilyl and triphenylsilyl-substituted BINOL (BINOL = [1,1′]binaphthalenyl-2.2′-diol) have been synthesized via alkane elimination from $La(CH\{SiMe_3\}_2)_3$. The energy required to twist the two aryloxide planes past each other in the biphenolate complex $[La\{CH(SiMe_3)_2\}\{1,1'\text{-}(2\text{-}OC_6H_2Bu^t_2\text{-}3,5)_2\}]$ is very low, so the two asymmetric isomers of the complex interconvert. However, in the complex $[La\{CH(SiMe_3)_2\}\{1,1'\text{-}(2\text{-}OC_{10}H_5SiPh_3\text{-}3)_2\}(OEt_2)]$ **3**, Fig. 2, the fused rings render the C_2-symmetric conformation rigid. The complex undergoes a clean CO insertion into the La–C bond, but no catalysis studies have been reported on these systems [27]. A lanthanum diiodide is readily made by treatment of the monopotassium salt HKBINOL with LaI_3, affording $LaI_2\{OC_{10}H_6–C_{10}H_6OH\}(THF)_2$ **4**, Fig. 2 [28]. Other than these, complexes of BINOL are generally formed as $M_3[Ln(BINOL)_3]$, where *M* = Li, Na, K. These very stable bimetallic complexes are effective catalysts for asymmetric aldol reactions and the enantioselective alkylation of aldehydes [29,30]. They

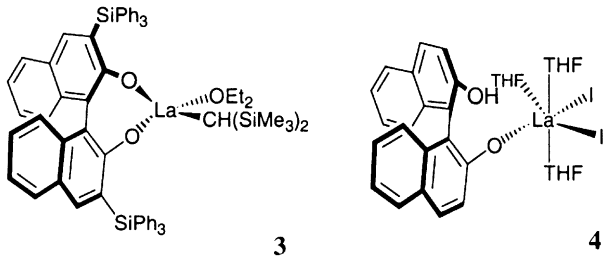
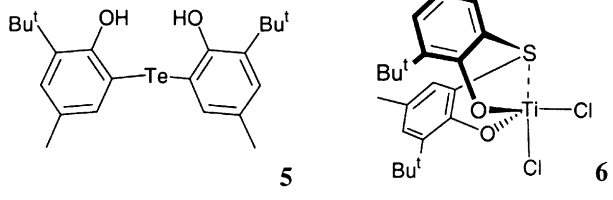


Fig. 2.

may be considered as a new class of bifunctional catalyst containing both a Lewis acidic site and a Brønsted base. This is demonstrated by the use of the complexes as promoters for the asymmetric nitroaldol reaction, the hydrophosphonylation of aldehydes and imines, and asymmetric Diels-Alder and Michael reactions [31].

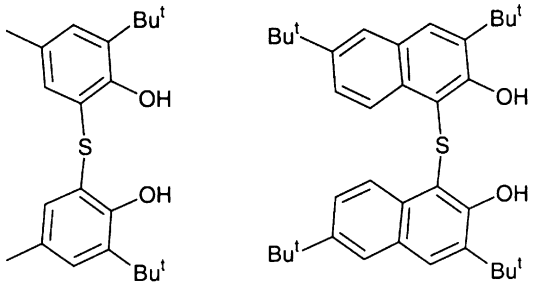
Recently, we have become interested in developing new alternative supporting ligands for *f*-element complexes—in particular complexes that have open coordination sites and can participate in reactivity such as small-molecule activation and catalysis. Aware of the thermodynamic stability of the lanthanide–aryloxide bond, but also the difficulty of retaining open, reactive coordination sites, we began to investigate atom-bridged biphenolates and binaphtholates which have been expanded by the formal insertion of an atom *X* as suitable dianionic supporting ligands for *f*-block metals. For convenience, these are denoted as [OXO] ligands, where the bracketed atoms are those capable of binding to the metal, but the type of bond is not defined. In the complexes described here the two O atoms derive from the biphenolate structure, and the ligand carries a dinegative charge. We wanted to know if the additional donor atom, *X*, would increase the ease of synthesis of lanthanide complexes of the ligand compared with the binolate and binaphtholate systems, and if the donor atom might then behave as a hemilabile functional group, by providing steric protection to a mononuclear complex, but not interfering with the subsequent reactivity of the Lewis acidic center. The *d*-block chemistry of bridged biphenolate ligands for $X = C$, N, P, S, Se and Te (**5**), Fig. 3, has already been studied in some depth [32]. The S-bridged biphenol is the most widely used example of this type, originally as a ligand in main group heterocycle chemistry [33], and more recently as a supporting ligand for some interesting *d*-block chemistry; Ti adducts catalyse alkene polymerization while Cu adducts catalyse the selective aerial oxidation of alcohols [34]. Related [OSO] ligands are also prevalent in the patent literature, since nickel complexes are effective antioxidants that are used to protect polymers from UV radiation [35].

Density functional theory has been used to predict the insertion barriers for ethene polymerization by cations of the form $[Ti[OSO]CH_3]^+$, the active species that is formed from $Ti[OSO]Cl_2$ **6**, Fig. 3, in the presence of methylalumoxane (MAO) cocatalyst. The results are in good agreement with experimental observations of these systems [36]. Of the three chalcogenide bridging atoms, it follows from the order of electron-donating capacity to the metal, S < Se < Te, that the ability of the bridging atom to lower the barrier to ethene insertion follows the order Te > Se > S. It follows that ligands with alkyl bridges that do not interact with the metal center form ineffective Group 4 alkene polymerization catalysts [37]. The most effective precatalysts are predicted to contain unsaturated CC backbones between the two anionic groups, and an $[OOO]^{2-}$ or an $[SSS]^{2-}$ set of donor atoms, although neither of these ligands has been synthesized to date [38]. Some studies of the PO, SO, SO_2, and even S_2-bridged systems have now been reported [39]. The macrocyclic analogue, tetrathiacalixarene has recently been shown to be a selective ligand for the UO_2^{2+} ion, but no lanthanide chemistry has been reported [40].



5 **6**

Fig. 3.



7 H_2L^S **8** H_2L^{SN}

Fig. 4.

Given the range of reactive metal complexes that have been made from the sulfur-bridged biphenol **7**, it is surprising that no Group 3 or *f*-element derivatives of this or any of the heteroatom-bridged ligands had been reported until now. In the last few months, we have been able to make some [OSO] derivatives of *Ln*(III) from across the f-block by both protonolysis and metathesis routes [41]; herein we focus on the Sm(III) chemistry of **7**, 1,1′-S(2-$HOC_6H_2Bu^t$-3-Me-5)$_2$, denoted H_2L^S shown in Fig. 4. We also describe how the use of new, larger ligands based on a *binaphtholate* framework, **8** in Fig. 4, 1,1′-S(2-$HOC_{10}H_4Bu^t_2$-3,6, denoted H_2L^{SN}, gives rise to subtle variations in the chemistry of the complexes.

2. Experimental details

All experimental procedures were carried out under an atmosphere of dry dinitrogen or argon, using standard Schlenk techniques (10^{-4} mbar) or in a glove box (M-BRAUN or Saffron). NMR spectra were recorded on a Bruker DPX 300 spectrometer, operating

frequency 300 MHz (^{1}H), 72 MHz (^{13}C), at 300 K. Chemical shifts are reported in parts per million, and referenced to residual proton resonances in d_6-benzene, and against external TMS. IR spectra were recorded on an Avatar 360 FT–IR spectrometer as nujol mulls between KBr discs, and mass spectra on a Kratos 320 spectrometer.

Solvents were freshly distilled from the appropriate drying reagent under dinitrogen, and were thoroughly degassed prior to use: diethylether and pentane from sodium/benzophenone, toluene from sodium, *n*-hexane, THF and benzene-d_6, from potassium. All chemicals were obtained from Aldrich Chemicals. The compounds $Sm(OAr)_3$, $H_2\mathbf{L}^{\mathbf{S}}$ $H_2\mathbf{L}^{\mathbf{SN}}$, **11**, **12**, and **13** were synthesized according to literature procedures [41,42].

X-ray data were collected using MoKα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART1000 CCD area detector diffractometer using ω scans. Structure solution and refinement was carried out using the SHELXTL suite of programs [43]. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 186033 for compound **9** and No. 186034 for compound **10**.

2.1. Attempted preparation of oxythiobis-3,6-di-tert-butyl-2-naphthol, preparation of 9

To a solution of thiobis-3,6-di-*tert*-butyl-2-naphthol (1.0 g, 1.85 mmol) in acetone was added H_2O_2 (1.0 ml, 9 mmol) and glacial acetic acid (0.51 ml). The reaction mixture was heated to reflux for 2 h, during which time the solution turned from colorless to orange. Removal of volatiles under reduced pressure and subsequent recrystallization from a minimum volume of *n*-hexane at −30°C yielded analytically pure needles of **9** in 22% yield (0.11 g), m.p. 123–125°C. Crystals of **9** suitable for single-crystal X-ray diffraction were grown at room temperature from a saturated *n*-hexane solution of the compound.

^{1}H NMR/$CDCl_3$ δ_H: 7.96 (d, 1H, 8-H $^3J_{HH}$ 8.1 Hz), 7.41 (dd, 1H 7-H $^3J_{HH}$ 8.1 Hz, $^4J_{HH}$ 1.84 Hz), 7.23 (d, 1H, 5-H $^4J_{HH}$ 1.84 Hz) s 7.22 (s, 1H, 4-H), 1.36 (s, 9H, 3-^{t}Bu), 1.32 (s, 9H, 6-^{t}Bu). δ_C: 181.6, 179.7, 160.7, 148.1, 140.0, 135.9, 130.2, 128.7, 127.5, 127.1 (naphthol), 35.9, 35.5 (quaternary), 31.2, 29.6 (Bu^t Me). ν (cm^{-1}) 1693w, 1662s, 1590m, 1267m. ES-MS m/z 271 (100%, $[M+H]^+$) HR ES–MS m/z 271.1694 (calc. for $[M+H]^+$ 271.1698). Anal. Calcd for $C_{18}H_{22}O_2$: C 79.96, H 8.20 Found: C 79.65 H 8.41.

2.2. Attempted preparation of dioxythiobis-3,6-di-tert-butyl-2-naphthol, preparation of 10

To a solution of thiobis-3,6-di-*tert*-butyl-2-naphthol (1.0 g, 1.85 mmol) in acetone was added H_2O_2 (2.0 ml, 18 mmol) and glacial acetic acid (3.06 ml). The reaction mixture was heated to reflux temperature for 2 h, during which time the solution turned from colorless to yellow. Removal of volatiles under reduced pressure and subsequent recrystallization from a minimum volume of chloroform at −30°C yielded analytically pure colorless crystalline 3,6-di-*tert*-butyl-1,2-dicarboxylic acid, **10**, 27% yield, 0.15 g. Crystals of **10** suitable for single-crystal X-ray diffraction were grown at room temperature from a saturated solution of the compound in chloroform.

^{1}H NMR/$CDCl_3$ δ: 7.99 (d, 1H, 8-H $^3J_{HH}$ 8.18 Hz), 7.34 (dd, 1H, 7-H $^3J_{HH}$ 8.25 Hz, $^4J_{HH}$ 1.62 Hz), 7.38 (d, 1H, 5-H $^4J_{HH}$ 1.62 Hz) s 7.13 (s, 1H, 4-H), 1.28 (s, 18H, 3-^{t}Bu, 6-^{t}Bu), 1.36 (s, 9H, 3-^{t}Bu), 1.32 (s, 9H, 6-^{t}Bu). ES-MS m/z 327 (24%, $[M+Na]^+$) HR ES-MS m/z 287.1641 (calc. for $[M–OH]^+$ 287.1647). Anal. Calcd. for $C_{18}H_{24}O_4$ C 71.03 H 7.95 S 0.00 found C 71.12 H 8.06 S 0.00.

2.3. Reaction of 13a with DME

In a Young's PTFE tap equipped NMR tube, two equivalents of DME (0.3 μL, 0.028 μmol) in d_6-benzene were added to a sunflower yellow d_6-benzene solution of **13a** at 300 K (3.0 mg, 0.014 μmol). An immediate color change to very pale yellow was observed due to the formation of a complex characterized as [Sm{1,1′-S(2-$OC_{10}H_4Bu^t_2$-3,6)$_2$} ($OC_6H_3Bu^t_2$-2,6) ($CH_3OC_2H_4OCH_3$), **14**. The ^{1}H NMR spectrum was recorded at this point, and remained unchanged after a further 24 h.

^{1}H NMR/C_6D_6 δ_H 8.47 (s, 2H, 5-H), 8.23 (d, 2H, 8-H), 7.95 (s, 2H, 4-H), 7.36 (d, 2H, 7-H), 6.98 (d, 2H, OAr-m), 7.73 (t, 1H, OAr-p), 1.12 (br s, 18H), 3.07, 1.35, 1.21 (s, 18H, 3-Bu^t, 6-Bu^t, OAr Bu^t) 0.80 (s, 4H, CH_2), 0.43p (s, 6H, CH_3), 1.57 (s, 18H).

2.4. Catalysis of monoacylation of meso-hydrobenzoin

Under an atmosphere of dry dinitrogen, a THF solution of *meso*-1,2-diphenyl-1,2-ethanediol (*meso*-hydrobenzoin) (2.4 ml) was treated with 10 equivalents of acetic anhydride and 10 mol% of a Sm(III) complex at 25°C. The extent of reaction was monitored over 24 h by regular extraction of aliquots for analysis by TLC (1:1 diethylether:hexane). At the end of the reaction period, a portion of ethyl acetate (25 ml) was added to the sample, and the solution washed successively with saturated $NaHCO_3$ (2 × 20 ml) and brine (20 ml). The organic solution was dried over $MgSO_4$, evaporated to dryness, and recrystallized from ethyl acetate/hexane. The spectroscopic data for the products were identical to that previously reported in the literature [44].

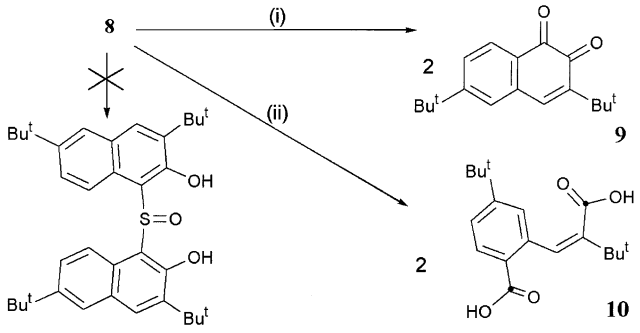
3. Results and discussion

The synthesis of the [OSO] ligand **7**, has been known since the 1980s, and involves the $ZnCl_2$-catalyzed coupling of 2-*tert*-butyl-4-methylphenol and sulfur dichloride. Under the same conditions, we have been able to convert 3,6-di-*tert*-butyl-2-naphthol into **8**, although we find the reaction is an order of magnitude faster. We considered that *f*-element derivatives of this larger [OSO] ligand might be easier to isolate as mononuclear complexes, and also that when bound to emissive centers such as Eu(III) or Tb(III) it might act as a light harnessing 'antenna' ligand, to generate complexes with interesting optical properties.

As one method of tuning the [OSO] ligand **8**, we have investigated oxidation of the sulfur bridge, **7** is selectively oxidized to yield ligands with an SO and an SO_2 bridge—both of which should bind as [OOO] ligands with reduced hemilability compared to an [OSO] ligand [45]. However, using the conditions identified for the mono- and di-oxygenation of **7**, **8** is instead converted into 1,2-naphthoquinone **9** and a dicarboxylate **10**, respectively, Scheme 1. In the cyclic voltammetry experiment, no electrochemical oxidation of **7** can be measured in the solvent window but an irreversible, multiple electron oxidation of **8** is observed at +0.78 V and a quasi-reversible oxidation at +0.81 V (Δ_{EP} 0.049 V) in THF.

The absence of clean oxidation chemistry of **8** has led us to investigate the lanthanide coordination chemistry of the simplest S-bridged, rather than the S=O or SO_2-bridged ligands, in the first instance.

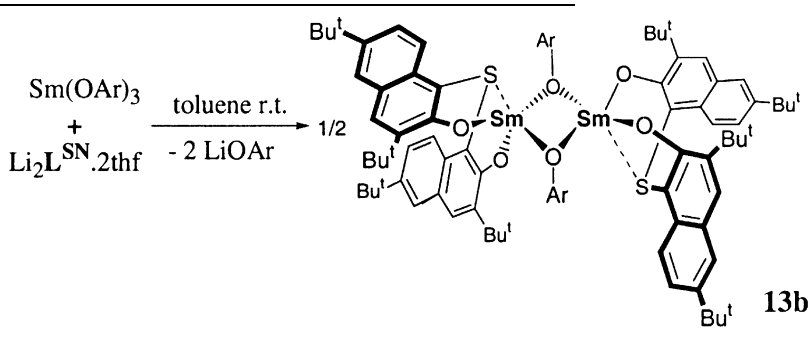
We have found that the reaction of $Sm(OC_6H_3Bu^t_2\text{-}2,6)_3$ with one equivalent of the biphenol **7** affords the complex $[Sm\{1,1'\text{-}S(2\text{-}OC_6H_2Bu^t\text{-}3\text{-}Me\text{-}5)_2\}(OAr)(THF)]$ ($OAr = OC_6H_3Bu^t_2$-2,6), **11** as bright yellow, hexane-soluble, air-sensitive crystals, Scheme 2 [41]; this was the first reported *f*-block complex of a sulfur-biphenolate, or any anionic [OSO] type ligand. The complex can be converted into a dinuclear, THF-free adduct **12** by heating in vacuo for a few hours. Similarly, the reaction of $Sm(OC_6H_3Bu^t_2\text{-}2,6)_3$ with an equivalent of binaphthol **8** affords sunflower yellow $[Sm\{1,1'\text{-}S(2\text{-}OC_{10}H_4Bu^t_2\text{-}3,6)_2\}(OC_6H_3Bu^t_2\text{-}2,6)]_2$, **13a**. The complexes are both readily handled in an inert atmosphere,



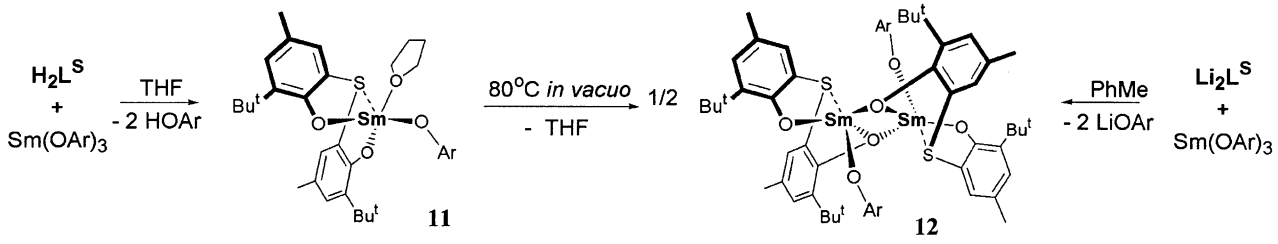
Scheme 1. (i) 9 mmol H_2O_2, glacial acetic acid, acetone, reflux 2 h. (ii) 18 mmol H_2O_2, glacial acetic acid, acetone, reflux 2 h.

thermally very stable, and soluble in common organic solvents including pentane. Attempts to sublime **12** or **13** to purity (pyrex tube, 10^{-5} mbar) have so far been unsuccessful. The most notable feature about both **12** and **13a** is that the two ring systems of the sulfur-bridged ligands are inequivalent in the NMR spectra recorded in benzene solution, and in the solid state as measured by single-crystal X-ray diffraction. One O anion of the chelating ligand bridges two metal centers, rendering the complexes C_2-symmetric. This is the first observation of this bridging mode of coordination for a metal complex of the [OSO] ligand.

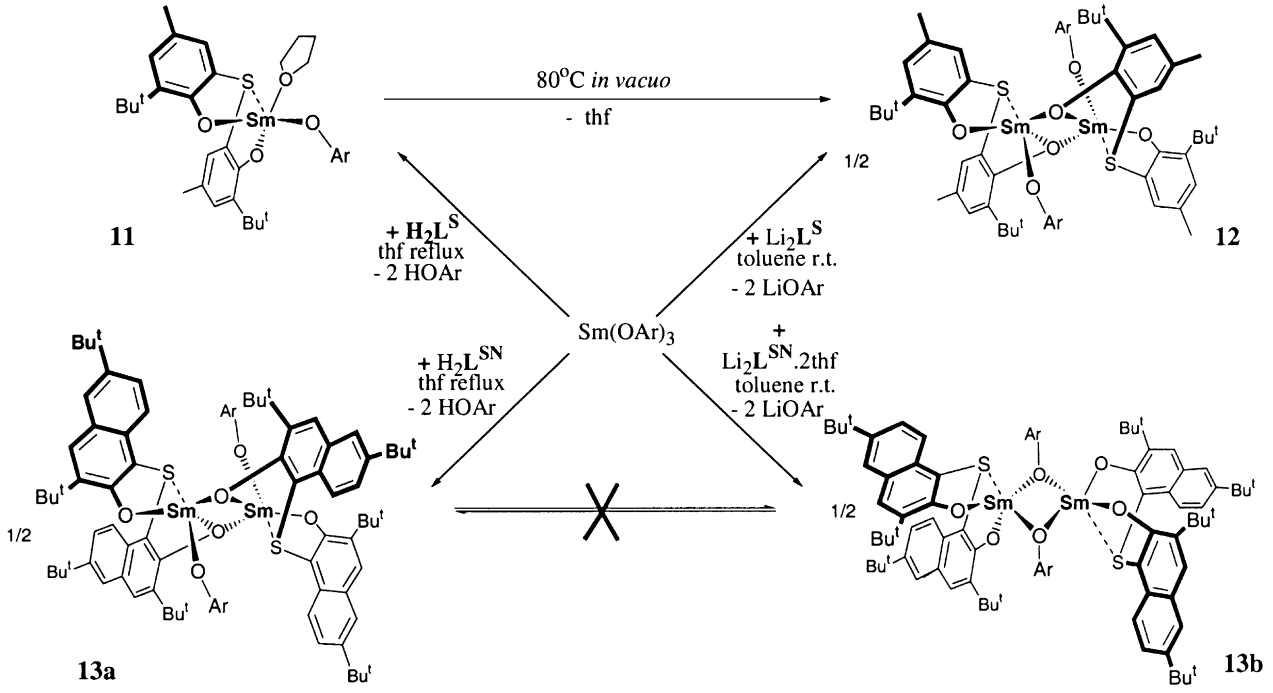
We have also investigated metathesis reactions to generate Sm(III) derivatives of these [OSO] ligands, since the reaction of $Sm(OAr)_3$ with a lithium phenoxide should eliminate the pentane-insoluble LiOAr as a byproduct, a procedure already shown to be of use in the reaction chemistry of the hexane-soluble lanthanide tris(aryloxides) [46]. The dilithium salts of the ligands, $1,1'\text{-}S(2\text{-}LiOC_6H_2Bu^t\text{-}3\text{-}Me\text{-}5)_2$ denoted $Li_2\mathbf{L^S}$ and $1,1'\text{-}S(2\text{-}LiOC_{10}H_4Bu^t_2\text{-}3,6)_2$, $Li_2\mathbf{L^{SN}}$, may be prepared most cleanly from the reaction of **7** or **8** with two equivalents of $LiN(SiMe_3)_2$ in diethylether and Li^nBu in THF, respectively [40]. Treatment of $Sm(OC_6H_3Bu^t_2\text{-}2,6)_3$ with base-free $Li_2\mathbf{L^S}$ affords two equivalents of $LiOC_6H_3Bu^t_2$-2,6 as a byproduct, and **12**, Scheme 2. Surprisingly, the reaction of $Sm(OC_6H_3Bu^t_2\text{-}2,6)_3$ with THF-solvated $Li_2\mathbf{L^{SN}}$ affords the C_{2v}-symmetric dinuclear complex **13b**, Eq. (1), rather than a THF-solvated complex analogous to **11**.



(1)



Scheme 2. Synthesis of Sm $\mathbf{L^S}$ derivatives from a homoleptic Sm(III) aryloxide complex.



Scheme 3. Synthetic routes to $\mathbf{L^S}$ and $\mathbf{L^{SN}}$ adducts of Sm(III).

The lack of any THF coordination by the binaphthol derivatives **13** provides the first observed difference in the metal chemistry of the two ligands. But a more interesting observation is that for Sm(III) we can selectively make the C_{2v}-symmetric analogue of the binaphtholate complex by a different procedure, so either a symmetric or asymmetric coordination of the ligand to Sm can be readily accessed. This chemistry is summarized in Scheme 3.

When all three potentially ligating atoms of the $\mathbf{L^S}$ and $\mathbf{L^{SN}}$ ligands are coordinated to a large metal cation the OSO functional groups are opened out, and the two ring systems are pushed together, and must either fold down against each other, reducing the CSC angle, or alternatively twist in opposite directions to reduce unfavorable steric interactions in the complexes (respectively (a) and (b) in Fig. 5). All the structurally characterized *d*-block complexes reported to date show a facially capping coordination environment as seen in **11** and **13b**, except for one Cu(II) derivative in which the tridentate ligand is close to a planar geometry about the pseudo-D_{4h} metal; a preferred geometry for Cu(II) [32].

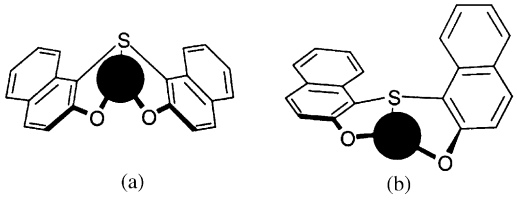


Fig. 5.

A single-crystal X-ray diffraction study of **13a** shows the twisted ligand conformation, Fig. 6. The two O atoms of the Sm_2O_2 core derive from naphthyloxides of two separate ligands, producing a tightly bound core with a short Sm–Sm distance of 3.6084(5) Å [47]. The Sm–S distance is 3.117(1) Å. This Sm–S distance is shorter than the maximum distance anticipated for a non-contact interaction between the two ions, implying that there is a significant Sm–S interaction in the solid

state [48]. A wide range of Sm–S distances have been measured in which the S donor is part of a covalently bound anionic ligand such as in tris(2,4,6-*tert*-butylphenylthiolato)Sm(III), ave. Sm–S 2.644 Å [49], or part of a delocalized $[-C(=S)(-S)]^-$ ligand such as in bis(hydrotris(3,5-dimethylpyrazolyl)borato)(diethyldithiocarbamato)Sm(III), ave. Sm–S 2.88 Å [50]. Two other structurally characterized lanthanide complexes, which exhibit similarly close Ln···S interactions with a neutral sulfur donor atom of a thioether have been reported recently. A complex of the facially capping thia-crown, La(9S3)I_3 $(CH_3CN)_2$ (9S3 = 1,4,7-trithiacyclononane), displays La–S distances in the solid state of between 3.0635(4) and 3.1263(4) [51]. These are longer than in the analogous U(III) adduct, indicating a weaker, but still significant interaction with the soft sulfur donors. The other is catena-sodium(bis(μ_5-thioglycolato)Nd(III)) [52], in which the central thioether of a dicarboxylate ligand forms a close (3.45 Å) contact with the neodymium cation resulting in a puckering of the nine-membered metallacyclic ring into two five-membered rings—a nearly identical conformation to that seen for **13**.

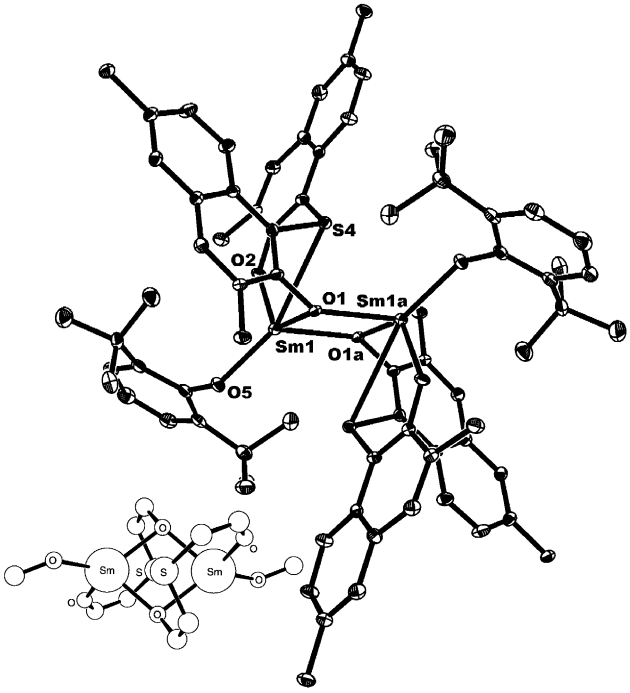


Fig. 6. ORTEP drawing of the molecular structure of **13a** (50% probability) with Me groups omitted. Inset, a Pluton view of the M_2O_2 core structure from above. Selected distances (Å) and angles (deg): Sm1–O5 2.138(3), Sm1–O2 2.157(3), Sm1–O1 2.392(3), Sm1-O1a 2.296(3), Sm1-S4 3.1172(11), Sm1–Sm1a 3.6084(5), O2–Sm1–O1 123.98(11), O2–Sm1–O1a 95.61(11).

The range of conformations of the phenolate and naphtholate ligands is shown diagrammatically in Fig. 7. Thus, it seems reasonable that the large samarium ion should accommodate the twisted conformation more readily than the symmetrical *fac* conformation. Since crude **13a** is heated to moderate (50°C) temperatures to remove eliminated phenol, perhaps the absence of heat in the synthesis of **13b** allows the sterically more crowded C_{2v} symmetric product to be isolated. We have seen no evidence for the interconversion of **13a** and **13b** in solution.

The 'wraparound' coordination that places the two aromatic planes perpendicular to each other, affords the complexes an intrinsic chirality, in a similar manner to BINOL complexes, but neither predetermined nor necessarily fixed at ambient temperatures. A variable temperature study of a d_8-toluene solution of the C_2-symmetric **13a** has been undertaken (see supplementary information). It shows that upon warming the solution above room temperature, in addition to the temperature-dependent paramagnetic shifts of the ligand ^{1}H resonances, the *ortho*-aryloxide resonances of the *tert*-butyl groups begin to coalesce. The coalescence temperature cannot be reached in standard NMR spectroscopic solvents, being in excess of 380 K, but the minimum free energy associated with this process is calculated as 69.7 kJ mol^{-1}. Importantly, over the range of temperatures studied it is clear that the dinuclear complex is neither dissociating nor undergoing any dynamic process that would destroy the asymmetry of the complex. The dynamic processes we can envisage

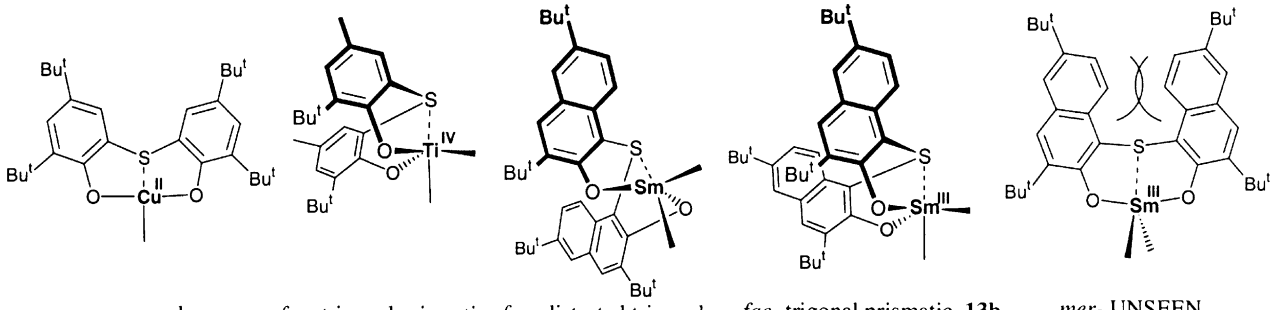
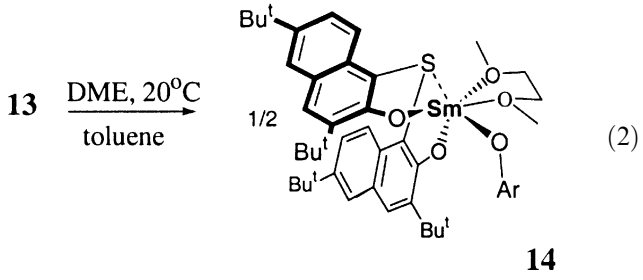


Fig. 7. Possible geometries for *d*- and *f*-block L^S and L^{SN} derivatives r_{ionic}[Cu(II)] 0.87, [Ti(IV)] 0.745, [Sm(III)] 1.098 Å [52].

include most probably the inversion of the [OSO] set at the metal via labilization of the sulfur, the bridging of alternative oxygen atoms from the ligand set, or the direct dissociation of the two halves of the dimer.

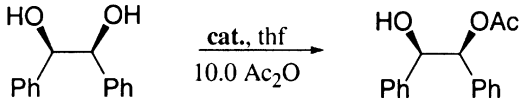
The reaction with DME in either toluene or benzene in a Young's tap NMR tube affords a pale yellow adduct $[Sm\{1,1'\text{-}S(2\text{-}OC_{10}H_4Bu^t_2\text{-}3,6)_2\}(OC_6H_3Bu^t_2\text{-}2,6)(CH_3OC_2H_4OCH_3)]$ **14**, in which at ambient temperature the ^1H chemical shifts of two naphthyl groups and the *tert*-butyl groups of the monodentate aryloxide are identical on the NMR timescale, although the DME resonances are broadened, Eq. (2).



(2)

14

We have studied the ability of the [OSO] complexes to catalyse the monoacylation, or desymmetrization, of 1,2 diols using *meso*-hydrobenzoin as a model substrate, Eq. (3). It has recently been discovered that lanthanide trihalides are more efficient promoters for this one-step reaction than traditional synthetic routes [53], which also are often multi-step or require specific substrate-dependent conditions.



(3)

meso-

A range of Sm(III) complexes and the simple tris(aryloxide), $Sm(OAr)_3$, were tested as promoters for this reaction, since nothing is currently known of the mechanism. Under an atmosphere of dry dinitrogen, a THF solution of a suitable test-substrate diol, *meso*-hydrobenzoin, was treated with an excess (10 equivalents) of acetic anhydride and a Sm(III) complex at 10 mol% at 25 °C. The mixture was magnetically stirred, and the extent of the reaction followed by TLC. The product distributions determined by ^1H NMR spectroscopy after 24 h (or 48 h) are gathered in Table 1.

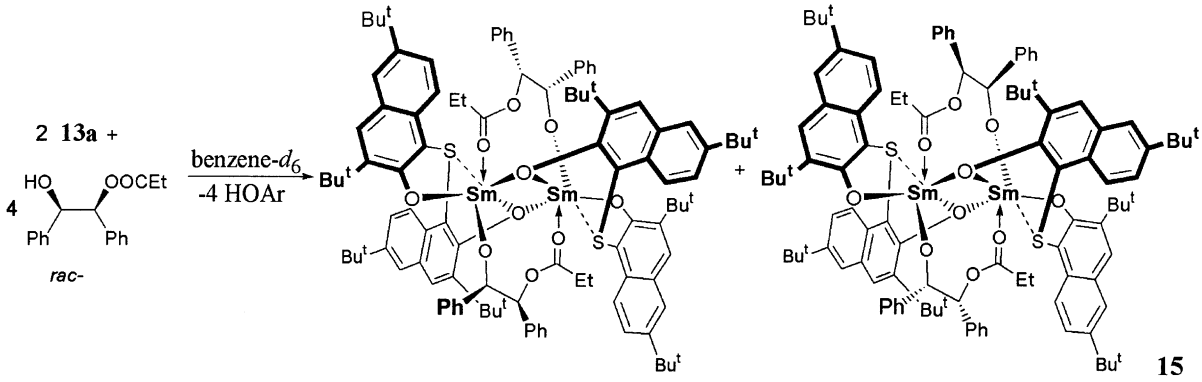
Anhydrous $SmCl_3$ is clearly an effective catalyst for this reaction, affording only a little overacylation of the diol, but is not particularly soluble in THF. The soluble trichloride is an unselective catalyst, whilst the soluble, but sterically encumbered $Sm(OAr)_3$ is a poor, slow catalyst, although still selective for the monoacylation. The former two compounds do not allow the reaction to be studied by NMR spectroscopy. It is clear that although the aryloxide-derived complexes are slow catalysts for the acylation reaction, the selectivity for monoacylation is complete, and if the reaction is allowed to proceed beyond 24 h at room temperature, the catalyst is still active.

Table 1
Product distributions from the use of selected lanthanide complexes as promoters for the monoacylation of *meso*-hydrobenzoin

Complex	Reaction time (h)	Ratio		
		Diol	Monoacyl	Diacyl
No catalyst	24	84	14	0
$SmCl_3$ (anhyd.)	24	11	86	3
$SmCl_3(THF)_3$	24	0	40	60
$Sm(OAr)_3$	24	66	34	0
12	24	50	50	0
12	48	34	66	0
13a	24	50	50	0

It appears that catalysts that are very soluble and very coordinatively unsaturated give fast but unselective acylation. These data are best explained by a reaction mechanism in which both the diol and the acylating agent coordinate to the Lewis acid metal before the OH is acylated. Our initial thoughts on the mechanism were that either the coordination of a diol is favored over coordination of the monoacylated product molecule (since both are THF-soluble and present in the mixture), which would disfavor the second acylation, or a situation exists where only an uncoordinated, but adjacent hydroxyl group is nucleophilic enough to attack the *Ln*-bound acylating agent, so if only one hydroxyl group is present the substrate is effectively deactivated upon complexation. If there is only one mode of catalysis, then our observations that the soluble, coordinatively unsaturated complexes give overacylation, and that the sterically encumbered complexes give only monoacylation products, both give weight to the former mechanism. A solution of **12** in dichloromethane is completely decomposed after stirring at room temperature for 24 h, preventing comparison with some of the $LnCl_3$-catalyzed reactions that have been studied previously.

Further reactivity studies have been undertaken to identify possible intermediates in this catalyzed reaction, and to help demonstrate how the acylating agent and monoacylated product fail to react further at the sterically encumbered catalysts, by treatment of paramagnetic **13a** with a racemic mono-propionate ester, Eq. (4). In this propionate adduct **15** the asymmetric naphtholate framework remains virtually unperturbed, and we find that two equivalents of either the *R*- or *S*-form of the ester bind to any one dimer. The substrate is sigma-bound to the metal as an alkoxide, so is undoubtedly not a real intermediate in the catalysis, but this result shows that there is a suitable metal-accessible cavity in the asymmetric dinuclear unit.



(4)

Work is now in progress to identify whether the optically pure analogues of **13a** are effective promoters for the stereoselective acylation of this *meso*-diol. We are also working to identify whether the ligand **8** binds solely in a bridging sense for the larger f-elements including Ce(III) and in a symmetrical *fac* conformation for Yb(III).

8. Conclusions

The sulfur-bridged dianionic [OSO] ligands derived from 2,2′-thiobis(6-*tert*-butyl-4-methylphen-2-ol) and thiobinaphthol 2,2′-thiobis(3,6-di-*tert*-butylnaphth-2-ol), form air-sensitive but thermally stable complexes of Sm(III) via a number of synthetically straightforward routes. The steric demands of the ligands on these large metals allow both *fac* and twisted conformations of the ligands to be isolated. In the latter, which is unprecedented in *d*-block chemistry to date, the ligands bridge to form C_2-symmetric dinuclear complexes. The dinuclear systems can be broken up into mononuclear Lewis base adducts with DME, but are not interconvertible on the NMR timescale up to 380 K in the absence of coordinating solvents. It is still unclear in these systems whether the S atom is acting as a hemilabile donor atom.

Acknowledgments

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Supplementary material available: Variable temperature NMR spectra of **13a**, full X-ray crystallographic data and atomic coordinates for **9** and **10**, cyclic voltammograms of **7** and **8** (16 pages).

References

[1] F.T. Edelmann, Angew. Chem. Int. Ed. 34 (1995) 2466.
[2] W.J. Evans, New. J. Chem. 19 (1995) 525.
[3] The melting points of the complexes are in the range 150 to 221°C, P.B. Hitchcock, M.F. Lappert, A. Singh, Chem. Commun. (1983) 1499;
C.L. Zhang, Y. Yao, Y. Luo, Q. Shen, J. Sun, Polyhedron 19 (2000) 2243.
[4] P.B. Hitchcock, M.F. Lappert, R.G. Smith, Inorg. Chim. Acta 139 (1987) 183;
H.A. Stecher, A. Sen, Inorg. Chem. 27 (1988) 1130.
[5] G.B. Deacon, P.E. Fanwick, A. Gitlits, I.P. Rothwell, B.W. Skelton, A.H. White, Eur. J. Inorg. Chem. (2001) 1505;
Y.M. Yao, Q. Shen, Y. Zhang, M.Q. Xue, J. Sun, Polyhedron 20 (2001) 3201.
[6] J. van den Hende, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, W.-P. Leung, T.C.W. Mak, S. Prashar, J. Chem. Soc. Dalton Trans. (1995) 1427;
R.C. Mehrotra, A. Singh, U.M. Tripathi, Chem. Rev. 91 (1991) 1287;
P.B. Hitchcock, M.F. Lappert, A. Singh, Chem. Commun. (1983) 1499;
G.B. Deacon, C.M. Forsyth, S. Nickel, J. Organomet. Chem. 647 (2002) 50;
G.B. Deacon, G. Meyer, D. Stellfeldt, Eur. J. Inorg. Chem. (2000) 1061.
[7] Y.-M. Yao, Q. Shen, Y. Zhang, M.-Q. Xue, J. Sun, Polyhedron 20 (2001) 3201.
[8] W. Chen, G. Yu, X. Bao, C. Bao, Huaxue Xuebao 43 (1985) 79.
[9] 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.
[10] W.J. Evans, M.A. Greci, J.W. Ziller, Inorg. Chem. 39 (2000) 3213;
W.J. Evans, M.A. Ansari, S.I. Khan, Organometallics 14 (1995) 558.
[11] D.L. Clark, J.C. Gordon, J.C. Huffman, R.L. Vincent-Hollis, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 5903;
G.B. Deacon, T. Feng, B.W. Skelton, A.H. White, Aust. J. Chem. 48 (1995) 741.
[12] W.J. Evans, R. Anwander, M.A. Ansari, J.W. Ziller, Inorg. Chem. 34 (1995) 5;
D.L. Clark, J.C. Gordon, J.C. Huffman, R.L. Vincent-Hollis, J.G. Watkin, B.D. Zwick, Inorg. Chem. 33 (1994) 5903;
D.L. Clark, G.B. Deacon, T. Feng, R.V. Hollis, B.L. Scott, B.W. Skelton, J.G. Watkin, A.H. White, Chem. Commun. (1996) 1729.
[13] J.R. van den Hende, P.B. Hitchcock, M.F. Lappert, Chem. Commun. (1994) 1413.
[14] G.B. Deacon, T. Feng, P. MacKinnon, R.H. Newnham, S. Nickel, B.W. Skelton, A.H. White, Aust. J. Chem. 46 (1993) 387; G.B. Deacon, P.B. Hitchcock, S.A. Holmes, M.F. Lappert, P. MacKinnon, R.H. Newnham, Chem. Commun. (1989) 935.

[15] W.J. Evans, R. Anwander, M.A. Ansari, J.W. Ziller, Inorg. Chem. 34 (1995) 5;
W.J. Evans, M.A. Greci, J.W. Ziller, J. Chem. Soc. Dalton Trans. (1997) 3035.
[16] Y.K. Gunko, F.T. Edelmann, Comm. Inorg. Chem. 19 (1997) 153.
[17] M.R. Burgstein, H. Berberich, P.W. Roesky, Chem. Eur. J. 7 (2001) 3078.
[18] M. Nishiura, Z.M. Hou, T. Koizumi, T. Imamoto, Y. Wakatsuki, Macromolecules 32 (1999) 8245.
[19] 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;
R.J. Butcher, D.L. Clark, J.C. Gordon, J.G. Watkin, J. Organomet. Chem. 577 (1999) 228;
Y. Yao, Q. Shen, J. Sun, F. Xue, Acta Crystallogr. C 54 (1998) 625;
Z. Hou, Y. Zhang, T. Yoshimura, Y. Wakatsuki, Organometallics 16 (1997) 2963;
W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, J. Organomet. Chem. 569 (1998) 89;
X.-G. Zhou, Z.-Z. Wu, Z.-S. Jin, J. Organomet. Chem. 431 (1992) 289; G.B. Deacon, S. Nickel, E.R.T. Tiekink, J. Organomet. Chem. 409 (1991) C1;
W.T. Klooster, L. Brammer, C.J. Schaverien, P.H.M. Budzelaar, J. Am. Chem. Soc. 121 (1999) 1381.
[20] W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, J. Organomet. Chem. 569 (1998) 89.
[21] Z.M. Hou, S. Kaita, Y. Wakatsuki, Pure Appl. Chem. 73 (2001) 291;
Z.M. Hou, Y. Wakatsuki, J. Alloys Compds. 303 (2000) 75.
[22] C.J. Schaverien, J. Mol. Catal. 90 (1994) 177.
[23] P.L. Arnold, A.J. Blake, S.N. Hall, B.D. Ward, C. Wilson, J. Chem. Soc. Dalton Trans. (2001) 488.
[24] V. Lorenz, A. Fischer, F.T. Edelmann, J. Organomet. Chem. 647 (2002) 245.
[25] J. Annand, H.C. Aspinall, J. Chem. Soc. Dalton Trans. (2000) 1867.
[26] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Gantner, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.
[27] C.J. Schaverien, N. Meijboom, A.G. Orpen, Chem. Commun. (1992) 124.
[28] N. Giuseppone, J. Collin, A. Domingos, I. Santos, J. Organomet. Chem. 590 (1999) 248.
[29] N. Yoshikawa, J.M.A. Yamada, J. Das, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 121 (1999) 4168.
[30] H.C. Aspinall, J.L.M. Dwyer, N. Greeves, A. Steiner, Organometallics 18 (1999) 1366;
H.C. Aspinall, J.F. Bickley, J.L.M. Dwyer, N. Greeves, R.V. Kelly, A. Steiner, Organometallics 19 (2000) 5416.
[31] M. Shibasaki, H. Sasai, T. Arai, Angew. Chem. Int. Ed. 36 (1997) 1237;
N. Yoshikawa, J.M.A. Yamada, J. Das, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 121 (1999) 4168.
[32] P. Chaudhuri, M. Hess, T. Weyhermuller, K. Wieghardt, Angew. Chem. Int. Ed. 38 (1999) 1095;
P. Chaudhuri, M. Hess, K. Hildenbrand, E. Bill, T. Weyhermuller, K. Wieghardt, Inorg. Chem. 38 (1999) 2781;
O.S. Filipenko, S.M. Aldoshin, E.P. Ivakhnenko, V.A. Valiulin, V.I. Minkin, Dokl. Akad. Nauk. 370 (2000) 345;
D.K. Petrikevich, V.A. Timoshchuk, O.I. Shadyro, O.T. Andreeva, V.I. Votyokov, V.E. Zhelobkovich, Khim.-Farm. Zh. 29 (1995) 32; K. Ohkata, T. Yano, T. Kuwaki, K. Akiba, Chem. Lett. (1990) 1721.
[33] T.K. Prakasha, R.O. Day, R.R. Holmes, J. Am. Chem. Soc. 115 (1993) 2690;
T.K. Prakasha, S. Srinivasan, A. Chandrasekaran, R.O. Day, R.R. Holmes, J. Am. Chem. Soc. 117 (1995) 10003;
R.M.L. Mercado, A. Chandrasekaran, R.O. Day, R.R. Holmes, Organometallics 18 (1999) 906.
[34] J. Okuda, E. Masoud, Makromol. Chem. Phys. 199 (1998) 543;
T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Makromol. Chem. Rapid Commun. 10 (1989) 349; Y. Yoshio, K. Masahiro, M. Koozi. M. Tatsuya US Patent 5043408 (1991); M. Hess, K. Wieghardt, P. Chaudhuri, US Patent 6153779 (2000).
[35] D.J. Carlsson, T. Suprunchuk, D.M. Wiles, US Patent 3871901 (1975).
[36] R.D. Froese, D.G. Musaev, K. Morokuma, Organometallics 18 (1999) 373.
[37] S. Fokken, T.P. Spaniol, J. Okuda, F.G. Sernetz, R. Mulhaupt, Organometallics 16 (1997) 4240;
Y. Nakayama, K. Watanabe, Y. Nakayama, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, Organometallics 19 (2000) 2498.
[38] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Gantner, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.
[39] J. Okuda, S. Fokken, T. Kleinhenn, T.P. Spaniol, Eur. J. Inorg. Chem. (2000) 1321;
J. Okuda, S. Fokken, H.C. Kang, W. Massa, Polyhedron 17 (1998) 943; F. Amor, S. Fokken, T. Kleinhenn, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 621 (2001) 3;
2,2′-PPh(4,6-But-C_6H_2OH) and 2,2′-PPh(=O)(4,6-But-C_6H_2OH), R. Siefert, T. Weyhermüller, P. Chaudhuri, J. Chem. Soc. Dalton Trans. 24 (2000) 4656.
[40] Z. Asfari, A. Bilyk, J.W.C. Dunlop, A.K. Hall, J.M. Harrowfield, M.W. Hosseini, B.W. Skelton, A.H. White, Angew. Chem. Int. Ed. 40 (2001) 721.
[41] P.L. Arnold, L.S. Natrajan, J.J. Hall, C. Wilson, J. Organomet. Chem. 647 (2002) 205.
[42] S.D. Pastor, J.D. Spivack, L.P. Steinhuebel, J. Heterocyclic. Chem. 21 (1984) 1285.
[43] Bruker, SHELXTL 5.10, Bruker AXS Inc., Madison, Wisconsin, USA, 1997;
G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467; G.M. Sheldrick, SHELXL97, University of Goettingen, Germany, 1997.
[44] P.C. Zhu, J. Lin, C.U. Pittman, J. Org. Chem. 60 (1995) 5729.
[45] J. Okuda, S. Fokken, H.-C. Kang, W. Massa, Polyhedron 17 (1998) 943;
C.R. Cornman, K.M. Geiser-Bush, J.W. Kamp, Inorg. Chem. 38 (1999) 4304;
A. Chandrasekarau, R.O. Day, R.R. Holmes, Organometallics 15 (1996) 3182.
[46] P.B. Hitchcock, M.F. Lappert, W.-P. Leung, L. Diansheng, T. Shun, Chem. Commun. (1993) 1386; P.B. Hitchcock, M.F. Lappert, R.G. Smith, R.A. Bartlett, P.P. Power, Chem. Commun. (1988) 1007.
[47] D.R. Click, B.L. Scott, J.G. Watkins, J. Chem. Cryst. 29 (1999) 921;
S. Daniele, L.G. Hubert-Pfalzgraf, J.-C. Daran, S. Halut, Polyhedron 13 (1994) 927.
[48] This maximum distance is defined as 0.15 Å longer than a single Sm–S bond, i.e. 3.148 Å (using the longest of the range of Sm–S distances), A. Bondi, J. Phys. Chem. 68 (1964) 441.
[49] B. Cetinskaya, P.B. Hitchcock, M.F. Lappert, R.G. Smith, Chem. Commun. (1992) 932.
[50] I. Lopes, A.C. Hillier, S.Y. Liu, A. Domingos, J. Ascenso, A. Galvao, A. Sella, N. Marques, Inorg. Chem. 40 (2001) 1116.
[51] L. Karmazin, M. Mazzanti, J. Pecaut, Chem. Commun. (2002) 654.
[52] C.J. Kepert, B.W. Skelton, A.H. White, Aust. J. Chem. 52 (1999) 617.

[53] J.H. Babler, M.J. Coghlan, Tetrahedron Lett. 20 (1979) 1971;
T. Nishiguchi, H.J. Taya, J. Am. Chem. Soc. 111 (1989) 9102;
M. Kinugasa, T. Harada, A. Oku, Tetrahedron Lett. 39 (1998) 4529;
H. Fujioka, Y. Nagatomi, N. Kotoku, H. Kitagawa, Y. Kita, Tetrahedron 56 (2000) 10141; N. Maezaki, M. Soejima, M. Takeda, A. Sakamoto, T. Tanaka, C. Iwata, Chem. Commun. (1994) 1345;
M. Oikawa, A. Wada, F. Okazaki, S. Kusumoto, J. Org. Chem. 61 (1996) 4469;
P.C. Zhu, J. Lin, C.U. Pittman Jr., J. Org. Chem. 60 (1995) 5729.