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STRUCTURAL CHARACTERIZATION AND REACTIVITY STUDIES OF THE SAMARIUM ARYLOXIDE COMPLEX $Sm(0-2,6-Pr_2^iC_6H_3)_3(THF)_2$

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Abstract—Reaction of the samarium aryloxide bis-THF adduct $Sm(OAr)_3(THF)_2$ (1; Ar = 2,6-Prⁱ₂C₆H₃) with two equivalents of pyridine produces the bis-pyridine complex Sm(OAr)₃py₂ (2) in 85% yield. Compound 1 also reacts with an excess of pyridine to form the tris-pyridine adduct Sm(OAr)₃py₃ (3) in excellent yield. Addition of one equivalent of KOAr to 1 leads to the isolation of the potassium salt K[Sm(OAr)₄] (4) in high yield. The salt 4 reacts with one equivalent of pyridine to form the mono-pyridine adduct K[Sm(OAr)₄py] (5). Compounds 1–5 have been characterized by ¹H NMR and IR spectroscopy, elemental analysis and, in the case of 1, by a single-crystal X-ray diffraction study. In the solid state, 1 adopts a trigonal bipyramidal structure in which THF ligands occupy axial sites. Sm—O distances to the aryloxide ligands average 2.14(2) Å, while those to THF ligands average 2.45(2) Å.

The alkoxide and aryloxide chemistry of scandium, yttrium and the lanthanide elements continues to be the subject of considerable interest, ^{1–16} due to the applicability of these complexes as precursors to ceramic materials,¹⁷ polymerization catalysts¹⁸ and catalysts for a range of organic transformations.¹⁹ A substantial body of knowledge has now been accumulated concerning the relationship between the steric demands of an alkoxide or aryloxide ligand and the degree of oligomerization of the

resulting molecular complex. In the case of lanthanide aryloxide species, numerous workers have reported that a considerable amount of control may be exerted upon the coordination number of the metal centre, and also the degree of oligomerization, through the selection of appropriate substituents on the arene ring. This strategy has led to the isolation of complexes exhibiting a number of interesting structural types, involving 2,6-dimethylphenoxide,^{2e,20} 2,6-diphenylphenoxide,²¹ 2,6di-tert-butylphenoxide,^{2d,22} 4-methylphenoxide²³ and binaphtholate²⁴ ligation.

We and others have recently demonstrated that

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the seemingly small change in steric demands between 2,6-di-tert-butylphenoxide and 2,6-di-isopropylphenoxide ligation leads to the isolation of *f*-element complexes of markedly differing structure and reactivity.^{12d,25} We have therefore initiated a detailed study of the structural and reaction chemistry of the lanthanide elements containing primarily 2,6-di-iso-propylphenoxide ligation, in order to further explore the often unique structures and properties which this ligand imparts upon its complexes.

Earlier publications have documented the isolation of the potassium salt complexes $K[Ln(OAr)_4]$ $(Ar = 2,6-Pr_2^iC_6H_3; Ln = La, Nd, Er)$, which exist in the solid state as either one-dimensional chains or two-dimensional sheets of $[Ln(OAr)_4]^-$ anions held together by means of potassium cations which interact with the arene rings of aryloxide ligands from adjacent anion units, as shown in L^{12a,e} We have also prepared homoleptic Ln(OAr)₃ complexes (Ln = La, Nd, Sm, Er) which differ sig- $Ln(O-2, 6-Bu_{2}^{t}C_{6}H_{3})_{3}$ nificantly from their analogues in that they exist both in the solid state and in solution as dimeric species through the agency of η^6 - π -arene bridges, as shown in II.^{12d,26}

These complexes are readily cleaved by the addition of Lewis bases such as THF to form monomeric $Ln(OAr)_3L_x$ (x = 2, 3) species.

In this paper we report upon the reaction chemistry of the samarium aryloxide complex Sm $(OAr)_3(THF)_2$ (1; Ar = 2,6- $Pr_2^iC_6H_3$), including ligand substitution reactions and its conversion to a member of the previously-described class of $K[Ln(OAr)_4]$ complexes.^{12a,e} The alkylation reaction of 1 with three equivalents of LiCH₂SiMe₃, which leads to the formation of the bis-alkyl complex [Li(THF)]₂[Sm(OAr)₃(CH₂SiMe₃)₂], containing a five-coordinate distorted trigonal bipyramidal carbon atom, has been described elsewhere.²⁷

RESULTS AND DISCUSSION

Synthesis and reactivity

Synthesis of the samarium aryloxide complex $Sm(OAr)_3(THF)_2$ (1; $Ar = 2,6-Pr_2^iC_6H_3$) via the preparative routes shown in eqs (1) and (2) has been described previously:^{12d}





$$SmCl_3 + 3KOAr \xrightarrow{\text{THF}} Sm(OAr)_3(THF)_2 + 3KCl$$
(1)
(1)

$$[Sm(OAr)_3]_2 + 4THF \longrightarrow 2Sm(OAr)_3(THF)_2$$
(1)
(2)

$$Ar = 2,6-Pr_{2}^{i}C_{6}H_{3}$$

Addition of one equivalent of pyridine to a toluene solution of **1** leads to a complex mixture of products which, based upon ¹H NMR evidence, appear to be of general formula $Sm(OAr)_3$ $(THF)_x(py)_y(x+y=2 \text{ or } 3)$. Attempts to isolate these complexes in pure form were unsuccessful. However, addition of exactly two equivalents of pyridine to toluene solutions of **1** results in a clean substitution reaction and the isolation of the bispyridine adduct $Sm(OAr)_3py_2$ (**2**) in good yield according to eq. (3). ¹H NMR integration and microanalytical data are consistent with the formulation of **2** with two molecules of coordinated pyridine.

$$Sm(OAr)_{3}(THF)_{2} + 2py \xrightarrow{\text{toluene}} Sm(OAr)_{3}py_{2} + 2THF \quad (3)$$
(2)
$$Ar = 2,6-Pr_{2}^{i}C_{6}H_{3}$$

Reaction of a toluene solution of 1 with an excess of pyridine allows the isolation of the tris-pyridine adduct $Sm(OAr)_3py_3$ (3) as a white microcrystalline solid [eq. (4)]. ¹H NMR integration and microanalytical data again support the proposed stoichiometry. A study of the low energy region of the IR spectrum of 3 mitigates against the formulation of this complex as a lattice solvate of the type $Sm(OAr)_3py_2 \cdot py$ (2 · py) (see below).

$$Sm(OAr)_{3}(THF)_{2} \xrightarrow{x_{5} p_{y}} followore for a product of the second sec$$

NMR tube experiments have shown that **3** is also formed from the reaction of the π -arene bridged dimeric species $[Sm(OAr)_3]_2^{12d}$ with excess pyridine in toluene solution, as shown in eq. (5):

$$[Sm(OAr)_{3}]_{2} \xrightarrow{xs py}{toluene} 2 Sm(OAr)_{3} py_{3}$$
(5)
(3)
$$Ar = 2,6-Pr_{2}^{i}C_{6}H_{3}$$

We have previously described the formation of the salt complexes $K[Ln(OAr)_4](Ln = La, Nd, Er,$ Lu) by reaction of anhydrous $LnCl_3$ with either three or four equivalents of potassium 2,6-di-isopropylphenoxide.^{12a,e} In order to ascertain whether complexes of this type could also be prepared via the reaction of 1 with one further equivalent of KOAr, a stirred THF solution of 1 was allowed to react with one equivalent of potassium aryloxide over a period of 2 days at room temperature. Extraction into toluene and slow evaporation of solvent led to the isolation of $K[Sm(OAr)_4]$ (4) in good yield, according to :

$$Sm(OAr)_{3}(THF)_{2} \xrightarrow{KOAr} K[Sm(OAr)_{4}] \quad (6)$$
(4)
$$Ar = 2,6 \cdot Pr_{2}^{i}C_{6}H_{3}$$

Microanalytical and ¹H NMR data fully support the formulation of **4** as a salt complex with no THF ligands within the coordination sphere of either the samarium or potassium metal centres.

Since we were unable to obtain X-ray quality crystals of 4, it was decided to attempt the preparation of a Lewis base adduct, which would possibly prove to be more amenable to the formation of single crystals. It was found that the interaction of a toluene solution of 4 with one equivalent of pyridine at room temperature led to the formation of a crystalline solid whose ¹H NMR and microanalytical data suggested to be the mono-pyridine adduct K[Sm(OAr)₄py] (5), as illustrated in eq. (7). A subsequent X-ray diffraction study (see below) showed 5 to possess a one-dimensional chain structure similar to that of Lewis base-free analogues,^{12a,c} with pyridine coordinated to the samarium metal centre.

$$K[Sm(OAr)_{4}] \xrightarrow{\text{1 equiv. py}}_{\text{toluene}} K[Sm(OAr)_{4}py] \quad (7)$$
(5)
$$Ar = 2,6-Pr_{2}^{i}C_{6}H_{3}$$

Solid state and molecular structures

 $Sm(O-2,6-Pr_2^iC_6H_3)_3(THF)_2$ (1). Data collection and processing parameters are presented in Table 1. Single crystals of 1 suitable for an X-ray diffraction study were grown by slow evaporation of a toluene solution in the drybox atmosphere, and the structure was solved from diffraction data collected at $-117^{\circ}C$. Selected bond lengths and angles are listed in Table 2. A ball-and-stick view of the overall molecular structure of 1, giving the atom numbering scheme used in the tables, is presented in Fig. 1. Compound 1 crystallizes in the

Empirical formula	$C_{44}H_{67}O_5Sm$
Crystal colour; habit	Pale yellow block
Crystal dimensions (mm)	$0.48 \times 0.16 \times 0.32$
Crystal system	Monoclinic
Space group	$P2_1$
Cell dimensions a (Å)	9.881(1)
b (Å)	19.467(3)
c (Å)	12.068(2)
β(°)	109.76(1)
Temperature (°C)	-117
Z (molecules per cell)	2
Volume (Å ³)	2184.8
D_{calc} (g cm ⁻³)	1.256
$\lambda (Mo-K_z)$	0.71069
Formula weight	826.41
Absorption coefficient (cm^{-1})	13.859
2θ range (°)	6-45
Measured reflections	5309
Unique intensities	2958
Observed refelctions	$2603 [F > 2.33\sigma(F)]$
$R(F)^a$	0.0286
$R_{w}(F)^{b}$	0.0285
Goodness-of-fit	0.882

Table 1. Summary of crystal data for $Sm(O-2,6-Pr_2^iC_6H_3)_3(THF)_2$ (1)

$${}^{a}R(F) = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$$

$${}^{b}R_{w}(F) = [\Sigma w(|F_{o}| - |F_{c}|)^{2} / \Sigma w|F_{o}|^{2}]^{1/2}; w = 1/\sigma^{2}(|F_{o}|)$$

Table 2. Selected bond distances (Å) and angles (°) for Sm(O-2,6-Pr₂ⁱC₆H₃)₃(THF)₂ (1)

Sm(1) - O(2)	2.179(5)		O(15)—C(16)	1.357(9)	
Sm(1)-O(15)	2.087(5)		O(28)—C(29)	1.339(9)	
Sm(1)—O(28)	2.166(5)		O(41)—C(42)	1.40(1)	
Sm(1)—O(41)	2.495(6)		O(41)—C(45)	1.38(1)	
Sm(1)—O(46)	2.407(6)		O(46)—C(47)	1.46(1)	
O(2) - C(3)	1.343(9)		O(46)C(50)	1.43(1)	
O(2) - Sm(1) - O(2)	(15)	135.4(2)	O(28)-Sm(1)-C) (41)	100.8(2)
O(2)— $Sm(1)$ — $O(2)$	(28)	110.9(2)	O(28)-Sm(1)-O)(46)	101.5(2)
O(2) - Sm(1) - O(2)	(41)	83.5(2)	O(41)—Sm(1)—C	D (46)	157.3(2)
O(2) - Sm(1) - O(2)	(46)	84.5(2)	Sm(1)O(2)C((3)	175.2(5)
O(15) - Sm(1) - O(15)	D(28)	113.7(2)	Sm(1)-O(15)-O	C(16)	173.9(5)
O(15) - Sm(1) - O(15)	D(41)	88.0(2)	Sm(1)-O(28)-O	C(29)	151.5(5)
O(15) - Sm(1) - O(15)	D(46)	87.2(2)			

monoclinic space group $P2_1$, and is isostructural with the related lanthanide complexes $Ln(OAr)_3$ $(THF)_2(Ln = Pr, Er, Gd, Lu)$, which have been structurally characterized.^{12d} The overall molecular structure consists of a samarium metal centre coordinated in a pseudo-trigonal bipyramidal fashion by three equatorial aryloxide and two axial THF ligands, as shown in Fig. 1. Sm—O distances for the aryloxide ligands in 1 average 2.14(2) Å, which is comparable to the Sm—O distances of 2.13(1), 2.08(2), 2.099(9) and 2.101(6) Å found for the aryloxide ligands in $(\eta$ -C₅Me₅)₂Sm(O-2,3,5,6-Me₄C₆H),²⁸ $[(\eta$ -C₅Me₅)₂Sm]₂(O₂C₁₆H₁₀),²⁹ $[(\eta$ -C₅Me₅)₂Sm(THF)]₂(O₂C₁₆H₁₀)²⁹ and Sm₂(O-2,6-Prⁱ₂C₆H₃)₆,^{12d} respectively. Sm—O distances for the THF ligands average 2.45(2) Å and can be compared with those found in other complexes containing Sm–THF ligation, including $[(\eta$ -C₅Me₅)₂Sm(THF)]₂(O₂C₁₆H₁₀),²⁹ $(\eta$ -C₅Me₅)₂Sm(CH₂C₆H₅) (THF)]₃₀ and $[(\eta$ -C₅Me₅)₂Sm(THF)]₂(μ -OSi-



Fig. 1. Ball-and-stick drawing emphasizing the trigonal bipyramidal coordination geometry of $Sm(O-2,6-Pr_2^iC_6H_3)_3(THF)_2$ (1), and giving the atom numbering scheme used in the tables. Iso-propyl methyl groups have been omitted for clarity.

Me₂OSiMe₂O),³⁰ which display Sm—O(THF) distances of 2.490(9), 2.498(5) and 2.465(5) Å, respectively. A common feature seen in 1 and in all other Ln(OAr)₃(THF)₂ structures is that two of the aryloxide ligands lie with their phenyl rings almost in the equatorial plane of the trigonal bipyramid, whereas the third aryloxide ligand [containing O(28)] is twisted noticeably out of this plane, presumably owing to the steric bulk of the di-iso-propylphenoxide ligands (Fig. 1). The Ln—O—C angle of this unique aryloxide ligand is $151.5(5)^{\circ}$, which is approximately 20° smaller than the average Ln—O—C angle for the other two aryloxide ligands [174.5(5)°].

Trigonal bipyramidal coordination has been observed previously in structurally characterized $Ln(OR)_3(L)_2$ complexes such as $Nd(OC-Bu_3^t)_3$ $(CH_3CN)_2$,^{14a} Ce(O-2,6-Bu_2^tC_6H_3)_3(CN-Bu^t)_2^{9a} and $[La(O-2,6-Ph_2C_6H_3)_3(THF)_2]$ • THF,^{21b} although the latter two complexes feature one axial and one equatorial Lewis base. The closely related fivecoordinate complex [Yb(O-2,6-Ph_2C_6H_3)_3(THF)_2]• THF, however, adopts a distorted square-based pyramidal structure in the solid state.^{21a}

 $K[Sm(O-2,6-Pr_2^iC_6H_3)_4py]$ (5). Single crystals of 5 suitable for an X-ray diffraction study were grown by slow evaporation of a toluene solution in the

drybox atmosphere. A ball-and-stick view of the molecular structure of 5 is shown in Fig. 2. Compound 5 crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters: a = 10.769(2), b = 21.919(4), c = 21.336(4) Å, $\beta = 101.55(3)^{\circ},$ V = 4934.3 Å³, $d_{calc} = 1.316$ g cm⁻³, Z = 4. Although the connectivity of the molecule could be established unambiguously, the quality of the Xray data was rather poor and thus we will not enter into any discussion of interatomic bond lengths and angles. The data reveal a quasi one-dimensional infinite chain structure in which five-coordinate pseudo-trigonal bipyramidal [Sm(OAr)₄py][−] anions are bridged through the agency of potassium-arene interactions between aryloxide ligands from adjacent [Sm(OAr)₄py]⁻ units. This structural motif is very similar to the structures of the related lanthanide aryloxide complexes $K[Ln(OAr)]_4$ (Ln = La, Nd, Er).^{12a,e} The potassium cation environment within 5 shows a marked similarity to the environment found in K[Nd(OAr)₄],^{12a} in that the primary interaction of the cation is with the oxygen of a phenoxide ligand and the remaining interactions occur with carbon atoms from two adjacent $[Ln(OAr)_4]^-$ units. It is noteworthy that the addition of pyridine to the Lewis base-free complex 4 leads only to coor-



Fig. 2. Ball-and-stick drawing of a section of the infinite-chain molecular structure of K[Sm(O-2,6-Prⁱ₂C₆H₃)₄py] (5). Iso-propyl methyl groups have been omitted for clarity.

dination of pyridine at the samarium metal centre, leaving the potassium cation with a mixed oxygen/carbon coordination sphere. Thus, the structure of **5** is a further example of the growing number of documented examples of potassium, and heavier alkali metal, cations interacting with arene moieties.^{3d,e,31}

Spectroscopic studies

NMR spectroscopy. Ambient temperature ¹H NMR spectra of **2** show resonances consistent with the presence of pyridine and aryloxide ligands in a 2:3 ratio, in agreement with the formulation of **2**. Only one aryloxide environment and one pyridine ligand environment are indicated by the ¹H NMR data. Based upon this spectroscopic data, and by analogy with structurally characterized Ln(OAr)₃ (THF)₂ complexes,^{12d} **2** is proposed to adopt a trigonal bipyramidal geometry with pyridine ligands occupying axial sites, as shown schematically in **III**. No evidence is seen for transformation of **2** into any other isomer in toluene-*d*₈ solution in the range from +80 to -80° C.



Addition of an excess of pyridine to toluene solutions of 1 leads to the formation of a species other than 2, as evidenced by its ¹H NMR spectrum. As well as significantly different chemical shifts from those observed in 2, integration of the ¹H NMR spectrum shows a 1:1 ratio of pyridine: aryloxide ligands. Microanalytical and spectroscopic data are consistent with the formulation of this complex as the tris-pyridine adduct 3. ¹H NMR spectroscopy shows that 3 may also be prepared by reaction of the π -arene bridged dimer Sm₂(OAr)₆^{12d} with excess pyridine [eq. (5)].

The observation of only one aryloxide and one pyridine ligand environment in the room temperature ¹H NMR spectrum of **3** is consistent either with a static fac isomer in solution, or a mer isomer in which a fluxional process renders the two types of aryloxide and pyridine ligands equivalent on the ¹H NMR time scale. Cooling of toluene- d_8 solutions of 3 to -80° C led to a complex low-temperature limiting spectrum, which is consistent with a fac structure in which rotation about the Sm-O-C and Sm-N bonds has been frozen out (as shown schematically in IV). A limiting low-temperature structure of this type is consistent with the fac geometry observed in the solid state of the yttrium aryloxide complex $Y(O-2,6-Me_2C_6H_3)_3(THF)_3^{20}$ and also the closely related lanthanum aryloxide species La(O-2,6- $Pr_2^iC_6H_3$)₃(NH₃)₄, in which one face of a fac La(OAr)₃(NH₃)₃ structure is capped by a fourth ammonia ligand.²⁶ Freezing out of rotation about both M-O-C and M-S-C bonds in sterically hindered *f*-element aryloxide and thiolate complexes has been observed previously.^{25a,32}



Assignment of resonances in the ¹H NMR spectra of **2** and **3** (especially those of the aromatic pyridine and aryloxide resonances) was greatly assisted by the use of two-dimensional $^{1}H^{-1}H$ COSY spectra. Although the paramagnetism of the Sm^{III} metal centre results in broadening of the resonances, it was found that standard acquisition parameters could be used to collect the correlation spectra.

Ambient temperature ¹H NMR spectra of 4 in benzene- d_6 show the presence of only one aryloxide environment and confirm the absence of THF from the coordination sphere of both potassium and samarium. The lack of THF precludes a structure such as that shown in V, which has been observed previously for a number of "ate" complexes of the lanthanide and actinide metals.^{2b,6,23,33} By analogy with the solid-state structures of the related complexes K[Ln(OAr)₄] (Ln = La, Nd, Er)^{12a,e} and 5 (see above), and based upon the striking similarity between solid-state IR spectra of these complexes and that of 4, we propose that 4 adopts a structure involving infinite chains of [Sm(OAr)₄]⁻ anions bridged by potassium-arene interactions between potassium cations and arene rings from adjacent $[Sm(OAr)_4]^-$ units.



Despite the fact that the solid state structure of 5 reveals asymmetry between the aryloxide ligands, it is notable that ¹H NMR spectra of 5 in benzene- d_6 reveal only one type of aryloxide ligand and one type of pyridine ligand, in a 4 : 1 ratio. The process which equivalences the aryloxide ligands in 5 could potentially involve C₆D₆ solvent molecules entering the coordination sphere of the potassium cations, or a rearrangement of the molecule in solution such that the potassium cations are coordinated by oxygen atoms of the phenoxide ligands.

IR spectroscopy. Solid-state (Nujol mull) IR spectra of compounds 2-5 in the region between 4000 and 400 cm^{-1} show only absorption bands characteristic of the coordinated ligands.³⁴ In the case of 3, IR spectroscopy may be used to support the formulation of this species as the tris-pyridine adduct rather than as a pyridine lattice solvate of 2 [i.e. $Sm(OAr)_3py_2 \cdot py$]. It is known that upon complex formation with a metal centre, pyridine vibrations in the high frequency region are not appreciably shifted, whereas the in-plane ring deformation mode is generally shifted from 604 cm^{-1} to higher energy.³⁵ In the case of **2**, the coordinated pyridine band is observed at 625 cm^{-1} , whereas in 3 the corresponding vibration is seen at 618 cm^{-1} . It may be expected that if **3** were a simple lattice solvate of formulation $Sm(OAr)_3py_2 \cdot py_2$ then two distinct IR bands would be observed at ca 625 cm^{-1} (for 2) and 604 cm^{-1} (for lattice pyridine).

CONCLUDING REMARKS

The 2,6-di-iso-propylphenoxide ligand has proven itself to be capable of providing a highly flexible coordination environment about a lanthanide metal centre. The Ln(OAr)₃ moiety has now been shown to support five-,^{12d} six- (see above) and seven-coordinate²⁶ geometries in the presence of a variety of Lewis bases, a π -arene bridged dimeric structure in the absence of additional Lewis base,^{12d} a five-coordinate bis-alkyl complex upon addition of two equivalents of LiCH₂SiMe₃,²⁷ and infinite-chain^{12a,e} or sheet^{12e} structures upon reaction with one equivalent of potassium aryloxide.

Efforts are currently underway to examine the differences in alkali metal coordination environments for the series of lanthanum aryloxide complexes M'[La(O-2,6-Pr_2ⁱC_6H_3)_4] (M' = Li, Na, K, Rb, Cs).

EXPERIMENTAL

General procedures and techniques

All manipulations were carried out under an atmosphere of oxygen-free UHP grade argon using

standard Schlenk techniques, or under oxygen-free helium in a Vacuum Atmospheres glovebox. 2,6-Di-iso-propylphenol was purchased from Aldrich and degassed before use. Potassium 2,6-di-isopropylphenoxide was prepared by the reaction of potassium hydride (Aldrich) with 2,6-diiso-propylphenol in THF. The preparation of Sm $(OAr)_3(THF)_2$ (1) has been described elsewhere.^{12d} Pyridine was distilled from CaH₂ under nitrogen. Solvents were degassed and distilled from Na-K alloy under nitrogen. Benzene- d_6 and toluene- d_8 were degassed, dried over Na-K alloy and then trap-to-trap distilled before use. Solvents were taken into the glovebox and a small amount tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22°C on a Brüker AF 250 or at 17°C on a Varian Unity 300 spectrometer in benzene- d_6 or toluene- d_8 . All 'H NMR chemical shifts are reported in ppm relative to the ¹H impurity in benzene- d_6 or toluene- d_8 set at δ 7.15 or 2.09, respectively. NMR spectra of paramagnetic lanthanide species are temperature dependent, thus it is important to note that the temperatures quoted represent average room temperatures and are approximate values. IR spectra were recorded on a Digilab FTS-40 spectrometer as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyser. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

Syntheses

 $Sm(O-2,6-Pr_2^iC_6H_3)_3py_2$ (2). To a pale yellow solution of 1 (0.642 g, 0.78 mmol) in toluene (40 cm³) was added pyridine (120 μ l, 1.48 mmol). After stirring the mixture overnight, the solution was concentrated to $ca \ 10 \ cm^3$ and allowed to evaporate slowly, leading to the formation of large pale crystals that were allowed to dry in the drybox atmosphere. Yield 0.56 g (85%). ¹H NMR (300 MHz, toluene- d_8): δ 7.71 (d, ${}^3J_{\text{HH}} =$ 7 Hz, 6H, meta OAr), 7.51 (t, ${}^{3}J_{HH} = 7$ Hz, 3H, para OAr), 6.05 (br, 4H, ortho py), 5.49 (t, ${}^{3}J_{HH} = 7$ Hz, 2H, para py), 4.95 (br m, 4H, meta py), 4.74 (br, 6H, CHMe₂), 1.38 $(d, {}^{3}J_{HH} = 6 \text{ Hz}, 36\text{H}, \text{CH}Me_{2})$. IR (cm^{-1}) : 1598 (m), 1585 (m), 1569 (w), 1443 (sh, s), 1430 (s), 1357 (m), 1327 (s), 1267 (s), 1214 (s), 1208 (s), 1153 (m), 1109 (m), 1096 (m), 1069 (m), 1060 (m), 1043 (m), 1036 (s), 1005 (m), 975 (vw), 954 (w), 933 (m), 918 (vw), 887 (s), 859 (s), 805 (w), 794 (w), 755 (s), 722 (m), 704 (s), 689 (s), 668 (w), 625 (m), 562 (m), 555

(m), 412 (m). Found : C, 65.1 ; H 7.5 ; N, 3.1. Calc. for $C_{46}H_{61}N_2O_3Sm$: C, 65.7 ; H, 7.3 ; N, 3.3%.

 $Sm(O-2,6-Pr_{2}^{i}C_{6}H_{3})_{3}py_{3}$ (3). To a solution of 1 (0.971 g, 1.17 mmol) in toluene (50 cm^3) was added $ca \ 2 \ cm^3$ of pyridine and the solution allowed to stir for 3 days. After this time the solution was concentrated to half its original volume and allowed to evaporate slowly. When dry, the white microcrystalline solid was collected. Yield 1.02 g (95%). ¹H NMR (300 MHz, benzene- d_6): δ 7.75 (d, ${}^{3}J_{HH} = 7$ Hz, 6H, meta OAr), 7.58 (t, ${}^{3}J_{HH} = 7$ Hz, 3H, para OAr), 6.93 (br, 6H, ortho py), 5.98 (br t, ${}^{3}J_{HH} = 7$ Hz, 3H, para py), 5.50 (br m, 6H, *meta* py), 4.52 (br, 6H, CHMe₂), 1.34 (d, ${}^{3}J_{HH} = 7$ Hz, 36H, CH Me_2). IR (cm⁻¹): 1593 (m), 1583 (m), 1568 (w), 1442 (s, sh), 1431 (s, sh), 1352 (m), 1341 (m), 1326 (m), 1281 (m), 1264 (s), 1217 (m), 1214 (m), 1207 (m), 1153 (m), 1140 (w), 1114 (m), 1095 (m), 1068 (m), 1059 (m), 1043 (m), 1033 (m), 1000 (m), 975 (vw), 933 (m), 918 (vw), 886 (s), 862 (m, sh), 855 (s), 804 (w), 796 (w), 763 (s, sh), 755 (s), 750 (s), 727 (s), 722 (s, sh), 705 (s), 694 (m, sh), 688 (s), 668 (m), 652 (w), 618 (s), 567 (s), 554 (m), 411 (m). Found: C, 67.0; H 6.9; N, 4.6. Calc. for C₅₁H₆₆N₃O₃Sm: C, 66.6; H, 7.2; N, 4.6%.

 $K[Sm(O-2,6-Pr_2^iC_6H_3)_4]$ (4). To a filtered THF solution (70 cm³) of KO-2,6- $Pr_2^iC_6H_3$ [prepared from KH (0.040)g, 1.0 mmol) and HO-2,6- $Pr_2^iC_6H_3$ (0.178 g, 1.00 mmol)] was added 1 (0.826 g, 1.00 mmol). The resulting solution was allowed to stir for 2 days, after which it was pumped to dryness, producing an oily solid. The solid was extracted with toluene, yielding a yellowish solution, and filtered through a Celite pad. The filtrate was pumped to dryness to give a pale yellow solid. Yield 0.89 g (99%). ¹H NMR (250 MHz, benzene d_6): δ 7.36 (d, ${}^{3}J_{HH} = 7$ Hz, 8H, meta OAr), 7.20 $(t, {}^{3}J_{HH} = 7 \text{ Hz}, 4\text{H}, para \text{ OAr}), 3.81 \text{ (br m, 8H,}$ $CHMe_2$), 0.72 (d, ${}^{3}J_{HH} = 5$ Hz, 48H, $CHMe_2$). IR (cm^{-1}) : 1592 (sh, w), 1581 (m), 1425 (s), 1334 (s), 1269 (s), 1209 (m), 1156 (w), 1111 (m), 1097 (w), 1062 (w), 1042 (m), 972 (vw), 957 (w), 934 (w), 919 (vw), 885 (m), 857 (s), 852 (s), 805 (w), 796 (w), 760 (s), 748 (s), 722 (m), 686 (m), 668 (w), 571 (m), 545 (m), 412 (w). Found : C, 63.4; H 7.5. Calc. for C48H68KO4Sm: C, 64.2; H, 7.6%.

K[Sm(O-2,6-Pr₁²C₆H₃)₄(py)] (5). Compound 4 (0.500 g, 0.56 mmol) was placed in 100 cm³ of toluene, yielding a pale yellow solution with some undissolved material, and then pyridine (45.5 μ l, 0.56 mmol) was added. After 5 min of stirring, all solid had dissolved. The solution was stirred overnight and then allowed to evaporate slowly, producing a microcrystalline solid which was collected by decantation of the mother liquor, washing with 2 × 5 cm³ aliquots of hexanes and pumping to dryness. Yield 0.33 g (60%). ¹H NMR (300 MHz, benzene- d_6): δ 7.66 (br, 2H, ortho py), 7.18 (d, ${}^{3}J_{\rm HH} = 7$ Hz, 8H, meta OAr), 7.02 (t, ${}^{3}J_{\rm HH} = 7$ Hz, 4H, para OAr), 6.37 (t, ${}^{3}J_{HH} = 8$ Hz, 1H, para py), 5.98 (br m, 2H, *meta* py), 3.17 (septet, ${}^{3}J_{HH} = 7$ Hz, 8H, CHMe₂), 0.88 (d, ${}^{3}J_{HH} = 7$ Hz, 48H, CHMe₂). IR (cm⁻¹): 1598 (m), 1587 (m, sh), 1583 (m), 1444 (s, sh), 1424 (s), 1364 (m, sh), 1360 (m, sh), 1336 (s), 1330 (s), 1269 (s), 1216 (m, sh), 1208 (m), 1154 (w), 1141 (w), 1109 (w), 1098 (w), 1071 (w), 1059 (w), 1043 (m), 1037 (m), 1005 (m), 951 (w), 940 (w), 936 (w), 919 (w), 888 (m), 863 (m, sh), 850 (s), 805 (w), 799 (w), 770 (m), 763 (s), 754 (s), 748 (s), 723 (w), 706 (m), 689 (m), 684 (m), 625 (m), 566 (m), 554 (m, sh), 551 (m, sh), 545 (m). Found: C, 65.1; H 8.4; N, 1.4. Calc. for C₅₃H₇₃KNO₄Sm: C, 65.1; H, 7.5; N, 1.4%.

Crystallographic details for $Sm(O-2,6-Pr_2C_6H_3)_3$ (THF)₂ (1)

General operating procedures have been described elsewhere.³⁶ The diffractometer utilized for data collection was designed and constructed locally at the IUMSC. The diffractometer consisted of a Picker four-circle goniostat equipped with a Furnas Monochromator (HOG crystal) and Picker X-ray generator interfaced to a Z80 micro-processor, and controlled by an RS232 Serial port on an IBM PC microcomputer. Motors are Slo-Syn stepping motors, and a special top/bottom–left/right slit assembly is used to align the crystal. All computations were performed on IBM compatible microcomputer systems.

The sample consisted of transparent crystals of varying morphologies. Several crystals were transferred to the cooling system, which was maintained at -171° C, and were observed to undergo a catastrophic phase transition. A suitable crystal was finally affixed to a glass fibre using silicone grease and transferred to the goniostat, where it was successfully cooled to $-117^{\circ}C$ for characterization and data collection. All handling was performed using standard inert atmosphere handling techniques. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and extinctions corresponding to one of the space groups $P2_1$ or $P2_1/m$. Subsequent solution and refinement of the structure revealed the non-centrosymmetric space group to be the correct choice.

Data were collected using a moving crystal, moving detector technique with fixed background counts at each extreme of the scan. Data were corrected for Lorentz and polarization effects and equivalent data averaged after correction for absorption. The structure was solved by direct methods (MULTAN78) and standard Fourier techniques. A difference map phased on the non-hydrogen atoms clearly located the position of most hydrogen atoms, and they were included in the final cycles of refinement as fixed atom contributors. A final difference Fourier was essentially featureless with the exception of several peaks of approximate density $0.7 \text{ e} \text{ Å}^{-3}$ in the vicinity of the samarium atom.

Supplementary material available. Atomic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

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