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Synthesis and X-ray crystal structures of the samarium mono(pentamethylcyclopentadienyl) aryloxide complexes (η-C_5Me_5)Sm(O-2,6-*t*-$Bu_2C_6H_3$)$_2$(THF) and [(η-C_5Me_5)Sm(O-2,6-*i*-$Pr_2C_6H_3$)$_3$Li(THF)]. Differences in metathesis chemistry of 2,6-di-*iso*-propylphenoxide and 2,6-di-*tert*-butylphenoxide ligands

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Abstract

The reaction of $SmCl_3$ with three equivalents of KO-2,6-*t*-$Bu_2C_6H_3$ in THF produces the tris(aryloxide) complex $Sm(OAr)_3$(THF) (Ar = 2,6-*t*-$Bu_2C_6H_3$, **1**). Complex **1** undergoes clean metathesis reaction with one equivalent of LiC_5Me_5 to form the mono(pentamethylcyclopentadienyl) aryloxide derivative (η-C_5Me_5)$Sm(OAr)_2$(THF) (**2**). In contrast, an analogous reaction of LiC_5Me_5 with the 2,6-di-*iso*-propylphenoxide complex $Sm(OAr^*)_3(THF)_2$ (Ar^* = 2,6-*i*-$Pr_2C_6H_3$, **3**) leads to overall addition of the alkali metal reagent, and isolation of the lithium-containing 'ate' complex [(η-C_5Me_5)Sm(OAr*)(μ-OAr*)$_2$Li(THF)] (**4**). Compounds **2** and **4** have been subjected to single-crystal X-ray diffraction studies. Complex **2** features a three-legged piano-stool geometry, with Sm–O distances to the aryloxide ligands of 2.133(6) and 2.188(6) Å, and a Sm–O(THF) distance of 2.435(7) Å. Complex **4** also exhibits a three-legged piano-stool geometry, with two of the aryloxide oxygen atoms coordinated to a lithium metal center. A THF ligand completes the coordination sphere of the lithium. The Sm–O bond lengths to the lithium-coordinated aryloxide oxygens (2.250(6) and 2.247(5) Å) are longer than the distance to the terminal aryloxide (Sm–O = 2.144(6) Å). The Li–O distances range from 1.876(17) to 1.945(18) Å. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Samarium; Aryloxide; Metathesis; Pentamethylcyclopentadienyl

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1. Introduction

In recent years, there has been a great deal of interest in the structure and reactivity of organometallic complexes of the f-elements [1,2]. Lanthanide complexes, in particular, have been shown to be extremely active catalysts and have found application in areas such as organic syntheses, olefin polymerization, catalytic hydrogenation and hydroamination, as well as in alkyne coupling reactions [3]. The most extensively investigated organolanthanide systems are those containing bis(pentamethylcyclopentadienyl) ligation [2]. The presence of these two bulky ligands can have dramatic consequences for the reactivity of the complexes toward potential substrates. One example of this behavior has been demonstrated by Marks and co-workers in the reaction of olefins with a series of complexes containing 'open' $(C_5Me_5)_2Ln$ and 'bridged' $Me_2Si(C_5Me_4)_2Ln$ fragments (Ln = Nd, Sm, Lu) [3c]. The bridged analogs were found to exhibit significant reactivity increases

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over the non-bridged analogs in reactions which proceed via sterically sensitive processes, such as olefin insertion into the (η-$C_5Me_5)_2$LnR and $Me_2Si(C_5Me_4)_2$-LnR metal–carbon σ bond. The conclusion of this study was that the bridging ring system allowed for an increase in the available coordination space around the metal center. As a consequence of these and other observations, it has been envisioned that the even greater steric and electronic unsaturation of mono(cyclopentadienyl) lanthanide systems, relative to their bis-ring counterparts, should make them desirable synthetic goals as potentially active catalysts [1,4].

Our recent research efforts have focused upon the chemistry of lanthanide metals containing primarily aryloxide ligation. We, and other groups, have noted that a significant degree of control over the coordination number and degree of oligomerization of the lanthanide complexes is available via the use of bulky substituents on the aryloxide ligand [5–11]. Owing to the relatively scarce nature of monomeric mono(pentamethylcyclopentadienyl) complexes containing aryloxide ligands, we set out to explore the possibility of preparing examples of this class via metathesis of an aryloxide ligand from tris(aryloxide) precursors using LiC_5Me_5. Lithium aryloxide formation (i.e. precipitation) has been used previously as a synthetic tool to replace a number of aryloxides with other ligand types, including alkyls and amides (Eqs. (1a) and (1b)) [1a].

$$Ln(OAr)_3 + 3LiR \rightarrow LnR_3 + 3LiOAr \qquad (1a)$$

Ln = La, Sm; Ar = 2,6-t-$Bu_2C_6H_3$; R = $CH(SiMe_3)_2$; Ref. [12]

$$Ln(OAr)_3 + MC_5Me_5 \rightarrow (\eta\text{-}C_5Me_5)Ln(OAr)_2 + MOAr \qquad (1b)$$

M = Li, Ln = La [13], Ce [14]; M = K, Ln = Y [15]
Ar = 2,6-t-$Bu_2C_6H_3$

We have previously reported, however, that the reaction of Sm(O-2,6-i-$Pr_2C_6H_3)_3(THF)_2$ with three equivalents of $LiCH_2SiMe_3$ did not lead to the desired metathesis reaction, but rather resulted in the addition of two equivalents of lithium alkyl to produce the mixed alkyl–aryloxide complex $[Li(THF)]_2$[Sm(O-2,6-i-$Pr_2C_6H_3)_3(CH_2SiMe_3)_2$] [7a]:

$$Ln(OAr)_3(THF)_2 + 3\,LiR \xrightarrow{THF} [Li(THF)]_2[Ln(OAr)_3R_2] + LiR \qquad (2)$$

Ln = Sm; Ar = 2,6-i-$Pr_2C_6H_3$; R = CH_2SiMe_3

Thus we set out to investigate whether lithium aryloxide metathesis could be used as a rational synthetic route to prepare mono(pentamethylcyclopentadienyl) samarium(III) complexes containing other bulky aryloxide ligands such as 2,6-di-*iso*-propylphenoxide, in addition to 2,6-di-*tert*-butylphenoxide. The isolation and characterization of the products from reactions of the tris(aryloxide) complexes Sm(O-2,6-t-$Bu_2C_6H_3)_3$-(THF) and Sm(O-2,6-i-$Pr_2C_6H_3)_3(THF)_2$ with one equivalent of LiC_5Me_5 are the subject of the present paper.

2. Results and discussion

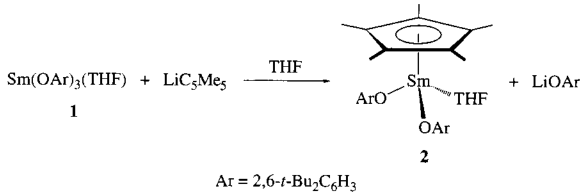
2.1. Synthesis and reactivity

The reaction of anhydrous samarium trichloride with three equivalents of KO-2,6-t-$Bu_2C_6H_3$ in THF leads to formation of the mono-THF adduct Sm(O-2,6-t-$Bu_2C_6H_3)_3$(THF) (**1**) in 28% yield (Eq. (3)). Similar tris-aryloxide complexes have been reported previously as both the solvent-free homoleptic species, and also as Lewis base adducts with coordinated acetonitrile and THF [6e,8a,16].

$$SmCl_3 + 3\,KOAr \xrightarrow{THF} Sm(OAr)_3(THF) + 3\,KCl \qquad (3)$$

Ar = 2,6-t-$Bu_2C_6H_3$

Metathesis reaction of **1** with one equivalent of LiC_5Me_5 proceeds smoothly to yield the mono(pentamethylcyclopentadienyl) samarium complex (η-C_5Me_5)Sm(O-2,6-t-$Bu_2C_6H_3)_2$(THF) (**2**) (Fig. 1) in good yield:



(4)

A similar synthetic route, employing Ln(O-2,6-t-$Bu_2C_6H_3)_3$ (Ln = Y, La, Ce) and one equivalent of KC_5Me_5 (Ln = Y) or LiC_5Me_5 (Ln = La, Ce), has been used previously to prepare the analogous base-free yttrium, lanthanum and cerium complexes (η-C_5Me_5)Ln(O-2,6-t-$Bu_2C_6H_3)_2$ (Ln = Y [15], La [13], Ce [14]). The fact that the lanthanum compound has been reported to react with THF to form a bis-THF adduct, (η-C_5Me_5)Ln(O-2,6-t-$Bu_2C_6H_3)_2(THF)_2$, rather than a mono-THF adduct analogous to **2**, presumably reflects the larger ionic radius of lanthanum compared to samarium. The ambient temperature ^{1}H-NMR spectrum of **2** in benzene-d_6 reveals a 2:1 ratio of aryloxide and Cp* ligands, and also upfield shifted resonances typical of a THF ligand bound to a samarium metal center. It has been reported that solutions of the lanthanum compound (η-C_5Me_5)La(O-2,6-t-$Bu_2C_6H_3)_2$ and the bis-THF adduct (η-C_5Me_5)Ln(O-2,6-t-$Bu_2C_6H_3)_2(THF)_2$ are both susceptible to ligand redis-

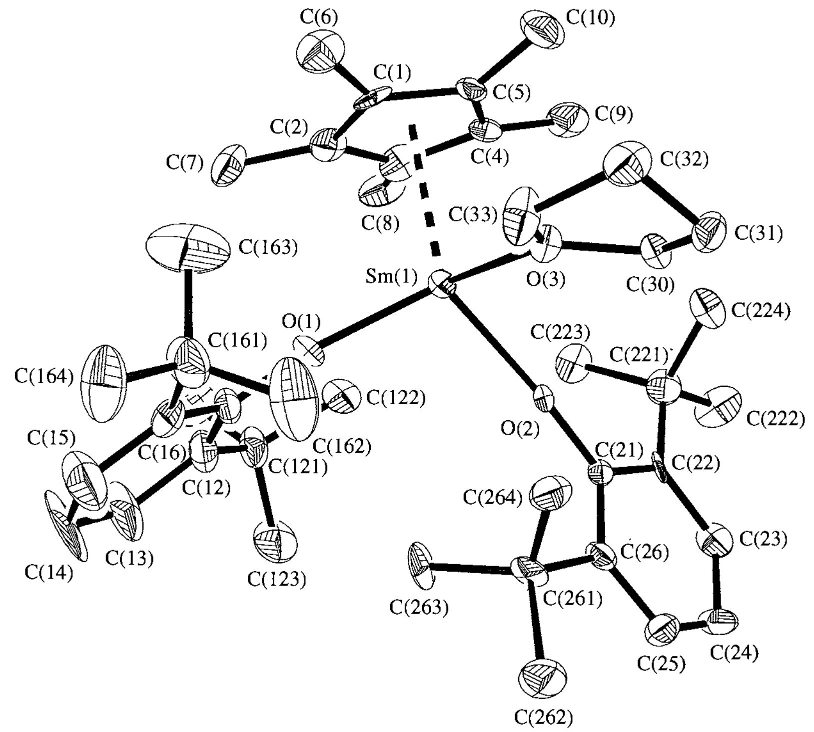
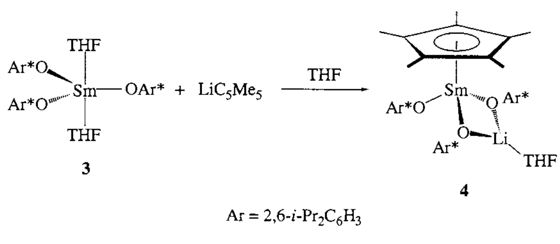


Fig. 1. ORTEP plot (40% probability ellipsoids) showing the molecular structure of (η-C_5Me_5)Sm(O-2,6-t-$Bu_2C_6H_3$)$_2$(THF) (**2**) giving the labeling scheme used in the Tables.

tribution to form a mixture of $Cp^*_2La(OAr)$, $Cp^*La(OAr)_2$ and $La(OAr)_3$ [13]. No evidence of similar solution behavior for **2** was observed. Complex **2** was found to crystallize from hexane with one molecule of lattice solvent per unit cell, and does not appear to be prone to solvent loss upon standing in the drybox atmosphere.

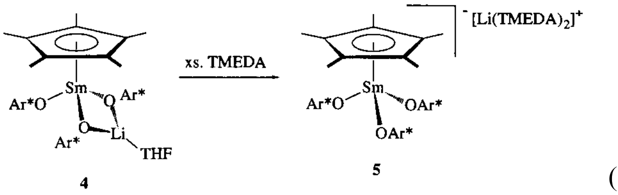
The synthesis of the Lewis base adduct Sm(O-2,6-i-$Pr_2C_6H_3$)$_3$(THF)$_2$ (**3**) has been described elsewhere [7a]. The reaction of **3** with one equivalent of LiC_5Me_5 does not produce the expected Cp*Sm(O-2,6-i-$Pr_2C_6H_3$)$_2$ species, but rather leads to overall addition of the lithium reagent to form the lithium 'ate' complex [(η-C_5Me_5)Sm(O-2,6-i-$Pr_2C_6H_3$)(μ-O-2,6-i-$Pr_2C_6H_3$)$_2$-Li(THF)] (**4**) as illustrated in Eq. (5).



(5)

Compound **4** (Fig. 2) is obtained as a yellow solid in good yield and is soluble in hydrocarbon solvents such as hexane and toluene. Compound **4** is found to crystallize from toluene with one lattice solvent molecule per formula unit. Removal of the mother liquor from a crystalline sample of **4** leads to rapid powdering and to analytical results (elemental analysis, ^{1}H-NMR integration) which show the presence of less than one solvent molecule per samarium moiety. ^{1}H-NMR spectra of **4** in benzene-d_6 show only one aryloxide ligand environment, indicative of rapid lithium exchange between pairs of 'legs' of the piano stool geometry. Rapid exchange of alkali metal cations between multiple alkoxide ligands has been a characteristic feature of previously-isolated f-element 'ate' complexes [7a,c,d].

Reaction of a hexane solution of **4** with an excess of TMEDA (tetramethylethylenediamine, $Me_2NCH_2CH_2$-NMe_2) leads to formation of a compound formulated as the salt complex **5** as shown in Eq. (6).



(6)

Microanalytical data and ^{1}H-NMR integration are consistent with the presence of two equivalents of TMEDA per formula unit. The formulation of **5** as a charge-separated salt complex is based upon the significant reduction in solubility in non-polar solvents of **5** as compared to **4** (**5** is found to be insoluble in hexane and toluene, soluble in THF and methylene chloride), and also the known ability of a bis-TMEDA coordination

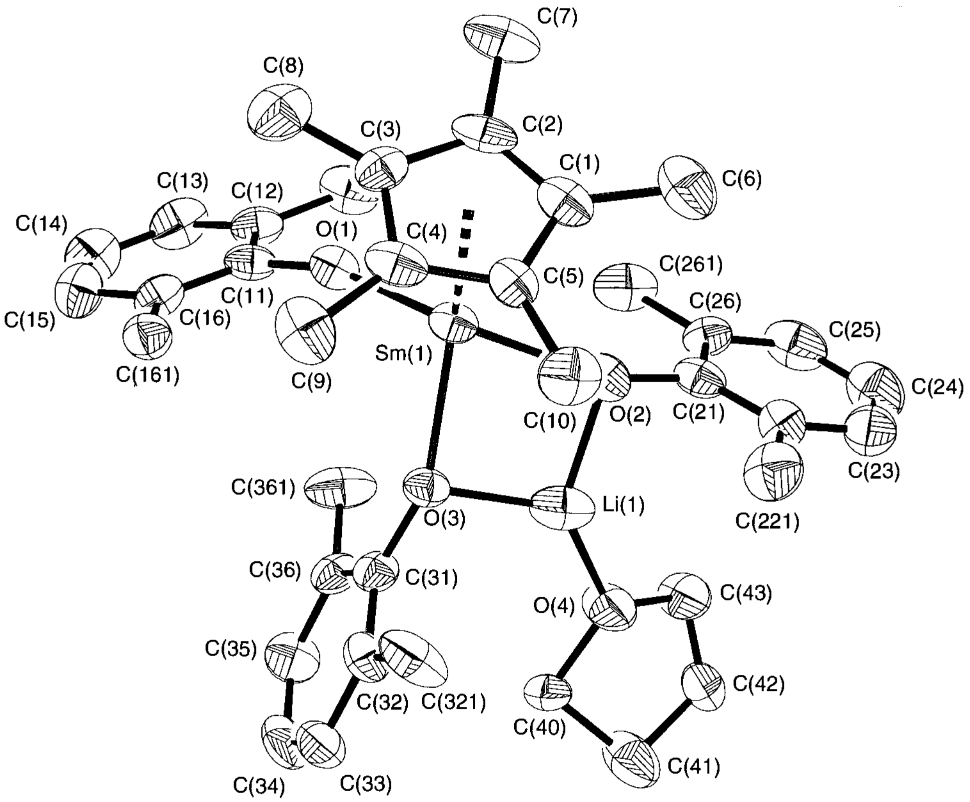


Fig. 2. ORTEP representation (40% probability ellipsoids) of the molecular structure of [(η-C_5Me_5)Sm(O-2,6-*i*-$Pr_2C_6H_3$)$_3$Li(THF)] (**4**) giving the labeling scheme used in the Tables. Methyl carbon atoms of the iso-propyl groups have been omitted for clarity.

environment to effectively separate a lithium cation from an anionic complex [17]. Attempts to grow single crystals of **5** for X-ray diffraction analysis were unsuccessful.

2.2. Solid state and molecular structures

The mono(pentamethylcyclopentadienyl) aryloxide complexes **2** and **4** have been examined by single crystal X-ray diffraction techniques. Data collection parameters are given in Table 1.

2.2.1. (η-C_5Me_5)Sm(O-2,6-t-$Bu_2C_6H_3$)$_2$(THF) · C_6H_{14} (2)

Single crystals of **2** suitable for an X-ray diffraction study were grown by slow evaporation of a hexane solution in the drybox atmosphere. Diffraction data were collected at −70°C. Fractional atomic coordinates and isotropic thermal parameters for **2** are presented in Table 2, while selected bond lengths and angles are listed in Table 3. The monomeric complex **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule of lattice hexane per formula unit. The geometry about the samarium metal center approximates a three-legged piano stool with two aryloxide ligands and a THF molecule constituting the 'legs' of the molecule.

The Sm–C bond distances to the cyclopentadienyl ligand average 2.762(10) Å, which is comparable to those observed in other samarium pentamethylcyclopentadienyl complexes [18,19]. The Sm–O(aryloxide) bond lengths of 2.133(6) and 2.188(6) Å are in the range previously observed for Sm(III)–O(aryloxide) interactions [7b,18,19a,20], while the Sm–O(THF) distance of 2.435(7) Å is also typical of those observed previously. The Sm–O–C(aryloxide) bond angles of 165.3(6) and 175.7(5)° differ considerably from those found in the base-free cerium analog (η-C_5Me_5)Ce(O-2,6-*t*-$Bu_2C_6H_3$)$_2$ [14]. In the cerium complex, Ce–O–C angles of 158.6(2) and 105.0(2)° were found, and a significant C–H···Ce interaction was observed with a methyl group on the aryloxide possessing the acute Ce–O–C angle. In the case of **2**, it is proposed that the presence of the coordinated THF ligand leads to greater steric saturation and decreased electrophilicity of the metal center, resulting in the absence of Sm–methyl contacts and the typically obtuse Sm–O–C(aryloxide) angles.

The two aryloxide ring planes differ markedly in their orientation with respect to the Cp* ligand. While the aryloxide containing O(1) is oriented with its ring plane roughly parallel to the Cp* plane, the aryloxide containing O(2) is twisted until almost perpendicular to the cyclopentadienyl ligand. As a result, the THF ligand is found to be situated significantly closer to the O(2) aryloxide (O(2)–Sm(1)–O(3) = 84.6(2)°) than the O(1) aryloxide (O(1)–Sm(1)–O(3) = 111.4(2)°), which has one of its *tert*-butyl groups directed toward the THF ligand.

2.2.2. [(η-C_5Me_5)Sm(O-2,6-*i*-$Pr_2C_6H_3$)$_3$Li(THF)] · C_7H_8 (4)

Single crystals of **4** suitable for X-ray diffraction analysis were grown by slow evaporation of a toluene solution in the drybox atmosphere. Diffraction data were collected at −100°C. Fractional atomic coordinates and isotropic thermal parameters for **4** are presented in Table 4, while selected bond lengths and angles are listed in Table 5. Compound **4** crystallizes in the monoclinic space group $P2_1/c$. The coordination geometry about the lanthanide metal center approximates a three-legged piano stool, the samarium atom being directly bound to three aryloxide ligands and a pentamethylcyclopentadienyl group. The overall molecular geometry is thus similar to that observed in the mono-pentamethylcyclopentadienyl lutetium tris(*tert*-butoxide) complex [(η-C_5Me_5)Lu(O-*t*-Bu)$_3$Li(TMEDA)] [21].

Table 1
Summary of crystal data

Compound[a]	**2**	**4**
Empirical formula	$C_{48}H_{79}O_3Sm$	$C_{57}H_{74}LiO_4Sm$
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
Unit cell dimension		
a (Å)	13.962(3)	10.878(5)
b (Å)	15.779(3)	13.869(10)
c (Å)	20.621(4)	35.94(2)
β (°)	90	93.06
Crystal size (mm)	0.57 × 0.35 × 0.35	0.53 × 0.34 × 0.32
Temperature (°C)	−70	−100
Z (mol/unit cell)	4	4
V (Å^3)	4543.3	5415
$D_{calc.}$ (g cm^{-3})	1.249	1.111
λ(Mo–K_α) (Å)	0.71073	0.71073
Formula weight	854.5	905.9
Index ranges	$0 \leq h \leq 16$, $0 \leq k \leq 18$, $-5 \leq l \leq 24$	$0 \leq h \leq 12$, $0 \leq k \leq 16$, $-42 \leq l \leq 42$
Absorption coefficient (cm^{-1})	13.29	11.22
Independent reflections	5542	9326
Observed reflections	4534 ($F > 4.0\sigma(F)$)	6503 ($F > 3.0\sigma(F)$)
R_1[b]	0.0491	0.0800
wR_2[b]	0.0626	0.0869

[a] **2** = (η-C_5Me_5)Sm(O-2,6-*t*-$Bu_2C_6H_3$)$_2$(THF) · C_6H_{14}; **4** = [(η-C_5Me_5)Sm(O-2,6-*i*-$Pr_2C_6H_3$)$_3$Li(THF)]·C_7H_8].

[b] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2
Fractional atomic coordinates (× 10^5) and equivalent isotropic displacement coefficients[a] (A^2 × 10^4) for (η-C_5Me_5)Sm(O-2,6-*t*-$Bu_2C_6H_3$)$_2$(THF) (**2**)

	x	y	z	U_{eq}
Sm(1)	18311(3)	17336(3)	84021(2)	177(1)
O(1)	27049(47)	7033(40)	80875(36)	240(20)
O(2)	4654(40)	15716(35)	78967(30)	163(18)
O(3)	20218(42)	29642(40)	77009(33)	222(20)
C(1)	32401(73)	24884(61)	91735(46)	236(27)
C(2)	29897(66)	17101(68)	94837(46)	274(28)
C(3)	20121(66)	18102(74)	97132(50)	312(31)
C(4)	16945(73)	26387(60)	95351(49)	249(29)
C(5)	24450(71)	30447(57)	92131(48)	213(30)
C(6)	42118(78)	27138(75)	89296(61)	371(38)
C(7)	36008(73)	9560(71)	95825(60)	348(36)
C(8)	15199(78)	12130(78)	101855(58)	405(38)
C(9)	8072(76)	30432(71)	97948(53)	347(35)
C(10)	24971(89)	39477(68)	90300(62)	382(39)
C(11)	30689(66)	−716(55)	79435(54)	262(29)
C(12)	26638(74)	−8057(68)	81917(67)	391(40)
C(121)	17934(78)	−9022(56)	86680(59)	320(32)
C(122)	12806(67)	−857(60)	88480(52)	265(30)
C(123)	10256(77)	−14945(64)	83739(72)	479(42)
C(124)	21488(92)	−12904(78)	93086(68)	518(46)
C(13)	30346(85)	−15956(65)	79862(86)	598(54)
C(14)	37913(102)	−16323(81)	75675(103)	891(80)
C(15)	42006(93)	−9131(80)	73353(86)	589(55)
C(16)	38626(67)	−1125(73)	75073(61)	344(36)
C(161)	43612(82)	6659(79)	72366(65)	418(40)
C(162)	36774(92)	11528(100)	67968(71)	651(56)
C(163)	47297(110)	12071(94)	77881(77)	703(60)
C(164)	52248(83)	4655(98)	67955(72)	609(55)
C(21)	−3673(59)	14080(52)	75745(48)	157(25)
C(22)	−12656(63)	15488(50)	78950(51)	163(28)
C(221)	−13551(71)	18730(66)	85916(56)	304(33)
C(222)	−24006(73)	18556(97)	88349(57)	425(41)
C(223)	−8085(70)	13170(69)	90706(51)	278(32)
C(224)	−10067(73)	27893(61)	86183(51)	284(32)
C(23)	−21066(64)	13937(62)	75520(58)	280(32)
C(24)	−20869(74)	11153(65)	69007(54)	295(32)
C(25)	−12151(65)	9947(57)	65990(59)	265(29)
C(26)	−3665(64)	11205(57)	69277(51)	201(27)
C(261)	5914(63)	9283(58)	65502(54)	249(28)
C(262)	3953(84)	6107(81)	58571(55)	402(38)
C(263)	11391(78)	2077(66)	68934(52)	291(32)
C(264)	11978(65)	17347(72)	64959(50)	321(30)
C(30)	11807(68)	35031(57)	75786(52)	234(30)
C(31)	14774(68)	41405(65)	70737(61)	303(34)
C(32)	25580(77)	41934(70)	71756(60)	350(37)
C(33)	28219(65)	32642(77)	73156(61)	370(35)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The samarium-ring carbon distances in **4** average 2.701(8) Å, comparable to those seen in **2**. The lithium cation displays a planar, three-coordinate geometry, being bound to two aryloxide oxygens (Li–O = 1.892(15) and 1.945(18) Å) and one THF ligand (Li–O = 1.876(17) Å). The two aryloxide oxygens bound to the lithium cation exhibit somewhat longer Sm–O distances (2.250(6) and 2.247(5) Å) than the terminal aryloxide (Sm–O = 2.144(6) Å). These longer bonding interactions are presumably due to a loss of electron density at oxygen upon forming the Sm–O–Li bridges, and can be compared to the average Sm–O distance of 2.266(7) Å found for the three lithium-coordinated aryloxide ligands in the complex $[Li(THF)]_2[Sm(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3(CH_2SiMe_3)_2]$ [7a]. The Sm–O distance for the terminal ligand is directly comparable to the average Sm–O distances of 2.08(2), 2.099(9), and 2.101(6) Å found for the terminal aryloxide ligands in $[(\eta\text{-}C_5Me_5)_2Sm]_2(O_2C_{16}H_{10})$ [19a], $[(\eta\text{-}C_5Me_5)_2Sm(THF)]_2(O_2C_{16}H_{10})$ [19a], and $Sm_2(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_6$ [7b].

Coordination of the lithium cation to O(2) and O(3) is found to dramatically reduce the O(2)–Sm(1)–O(3) angle from an expected tetrahedral value down to 76.9(2)°. Significant differences in orientation of the aryloxide ring planes also result in the terminal aryloxide ligand being situated closer to the O(3) ligand (O(1)–Sm(1)–O(3) = 98.1(2)°) than the O(2) moiety (O(1)–Sm(1)–O(2) = 126.2(2)°), which has one of its *iso*-propyl groups oriented directly toward the terminal aryloxide. Angles about the lithium cation sum to 358.7°, indicating an almost perfect trigonal planar coordination environment.

3. Concluding remarks

We have described the results of attempted metathesis reactions of samarium tris(aryloxide) complexes with one equivalent of lithium pentamethylcyclopentadienide. In the case where the aryloxide ligand is 2,6-di-*tert*-butylphenoxide we observe a clean metathesis reaction, with elimination of LiOAr, and the formation of the desired neutral mono-pentamethylcyclopentadienyl product. This result is consistent with the observations of other workers, in which the 2,6-di-*tert*-butylphenoxide ligand was found to undergo successful metathesis reactions with alkyllithium reagents

Table 3
Selected bond lengths (Å) and angles (°) for $(\eta\text{-}C_5Me_5)Sm(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2(THF)$ (**2**)

Bond lengths (Å)			
Sm(1)–O(1)	2.133(6)	Sm(1)–O(2)	2.188(6)
Sm(1)–O(3)	2.435(7)	Sm(1)–C(1)	2.796(10)
Sm(1)–C(2)	2.755(9)	Sm(1)–C(3)	2.718(10)
Sm(1)–C(4)	2.745(10)	Sm(1)–C(5)	2.795(9)
Bond angles (°)			
O(1)–Sm(1)–O(2)	105.3(2)	O(2)–Sm(1)–O(3)	84.6(2)
O(1)–Sm(1)–O(3)	111.4(2)	Sm(1)–O(1)–C(11)	165.3(6)
Sm(1)–O(2)–C(21)	175.7(5)		

Table 4
Fractional atomic coordinates ($\times 10^5$) and isotropic thermal parameters ($\times 10^4$) for $[(\eta\text{-}C_5Me_5)Sm(OAr^*)(\mu\text{-}OAr^*)_2Li(THF)]$ (**4**) ($Ar^* = 2,6\text{-}i\text{-}Pr_2C_6H_3$)[a]

	x	y	z	U_{eq}
Sm(1)	11389(3)	7132(4)	13888(1)	317(1)
Li(1)	30890(132)	22856(133)	15395(41)	541(28)
O(1)	17958(42)	−6307(45)	11814(13)	364(16)
O(2)	16941(47)	21926(45)	12036(13)	390(17)
O(3)	27580(43)	10637(39)	17798(13)	335(16)
O(4)	44872(54)	30790(51)	15720(17)	610(20)
C(1)	−12331(66)	13306(75)	12981(21)	389(21)
C(2)	−12572(67)	4078(70)	11386(21)	411(22)
C(3)	−10186(67)	−2730(68)	14275(22)	347(21)
C(4)	−8270(67)	2386(75)	17700(20)	374(21)
C(5)	−9810(65)	12287(71)	16883(20)	323(20)
C(6)	−15094(78)	22661(73)	10895(24)	577(24)
C(7)	−15561(82)	1627(84)	7382(22)	635(24)
C(8)	−10445(78)	−13327(74)	13719(28)	572(25)
C(9)	−6185(76)	−1851(75)	21554(22)	520(23)
C(10)	−9507(76)	20175(70)	19810(22)	491(23)
C(11)	23919(67)	−14805(66)	11636(20)	344(21)
C(12)	29260(71)	−17302(71)	8255(22)	419(22)
C(121)	27219(81)	−10674(79)	4925(22)	567(24)
C(122)	14632(91)	−12664(97)	3045(26)	858(26)
C(123)	37393(92)	−11063(86)	2101(28)	792(26)
C(13)	35713(80)	−25785(73)	8030(26)	543(24)
C(14)	37270(83)	−31808(79)	11104(27)	587(25)
C(15)	31916(79)	−29646(73)	14382(25)	513(24)
C(16)	25225(73)	−21023(67)	14745(22)	406(22)
C(161)	19264(76)	−18575(68)	18240(20)	421(22)
C(162)	28687(86)	−15780(76)	21457(23)	595(24)
C(163)	11451(82)	−27030(75)	19613(26)	614(24)
C(21)	17721(67)	30191(71)	9978(20)	375(21)
C(22)	14656(75)	39115(66)	11432(22)	383(22)
C(221)	9514(84)	39793(77)	15169(26)	568(25)
C(222)	−2238(93)	45975(83)	15147(34)	845(27)
C(223)	18785(104)	43761(98)	18141(28)	972(27)
C(23)	16818(81)	47296(77)	9400(25)	515(24)
C(24)	21592(89)	46846(88)	5941(28)	667(25)
C(25)	24231(84)	37803(87)	4446(24)	595(24)
C(26)	22416(71)	29203(68)	6400(20)	382(21)
C(261)	25013(79)	19513(83)	4798(25)	606(24)
C(262)	35528(112)	19336(101)	2181(32)	1093(28)
C(263)	13493(114)	15914(111)	2918(40)	1479(29)
C(31)	37865(64)	9162(61)	20072(21)	344(21)
C(32)	37960(71)	12088(68)	23809(22)	401(21)
C(321)	26744(83)	16784(83)	25386(22)	608(24)
C(322)	20177(146)	10856(139)	27793(60)	702(30)
C(323)	30672(173)	27015(147)	27421(54)	833(30)
C(33)	48705(77)	11031(66)	26025(22)	453(22)
C(34)	59121(73)	6988(75)	24599(25)	537(23)
C(35)	58873(73)	3826(70)	20961(25)	505(23)
C(36)	48355(68)	4730(61)	18640(22)	383(22)
C(361)	48028(76)	1130(83)	14677(26)	609(24)
C(362)	55405(84)	−8002(82)	14298(33)	864(26)
C(363)	52565(90)	8393(91)	11987(27)	861(26)
C(40)	56616(158)	28650(145)	18204(49)	440(29)
C(41)	62329(94)	38790(87)	18383(30)	742(26)
C(42)	58725(173)	42756(166)	14419(54)	496(30)
C(43)	48488(89)	37372(80)	12905(26)	640(25)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[12,13,15,22,23]. In the case of attempted metathesis reaction involving the 2,6-di-*iso*-propylphenoxide ligand, however, the observation of an addition rather than a metathesis reaction reinforces the mode of reactivity previously observed [8a].

Previously [7a], we had interpreted the differences in observed reactivity of alkyllithium reagents with lanthanide aryloxide complexes (compare Eqs. (1a) and (2)) in terms of two contributing factors: (i) the reduced steric requirement of the 2,6-di-*iso*-propylphenoxide ligand, compared with 2,6-di-*t*-butylphenoxide, allows greater freedom for coordination of three aryloxide ligands simultaneously to the lanthanide metal center, and (ii) the solubility of lithium 2,6-di-*iso*-propylphenoxide in THF is considerably greater than that of lithium 2,6-di-*tert*-butylphenoxide, thus the driving force for precipitation of the lithium aryloxide is significantly lower. The first of these factors appears to be supported by very recent results, in which Evans et al. reported that the reaction of the 2,6-dimethyl substituted aryloxide complex $Y(O\text{-}2,6\text{-}Me_2C_6H_3)_3(THF)_2$ with one equivalent of NaC_5Me_5 led to the formation of the discrete ion pair complex $[Na(THF)_6][(\eta\text{-}C_5Me_5)Y(O\text{-}2,6\text{-}Me_2C_6H_3)_3]$ [24]. Thus the use of a less sterically demanding aryloxide appears to favor the formation of an addition, rather than a metathesis, product. The extent to which the solubility of the lithium aryloxide salt controls the reaction is still in question. However, it appears that the use of a less polar reaction solvent (e.g. toluene) favors metathesis reaction (by encouraging precipitation of alkali metal aryloxide), whereas use of a polar, coordinating solvent such as THF encourages solvation of the alkali metal cation and the formation of addition, or 'ate' complexes. Further studies in this area are currently in progress.

Table 5
Selected bond distances (Å) and angles (°) for $[(\eta\text{-}C_5Me_5)Sm(OAr^*)(\mu\text{-}OAr^*)_2Li(THF)]$ (**4**) ($Ar^* = 2,6\text{-}i\text{-}Pr_2C_6H_3$)

Bond lengths (Å)			
Sm(1)–O(1)	2.144(6)	Sm(1)–O(2)	2.250(6)
Sm(1)–O(3)	2.247(5)	Sm(1)–C(1)	2.722(8)
Sm(1)–C(2)	2.744(8)	Sm(1)–C(3)	2.726(8)
Sm(1)–C(4)	2.683(8)	Sm(1)–C(5)	2.693(8)
O(2)–Li(1)	1.892(15)	O(3)–Li(1)	1.945(18)
O(4)–Li(1)	1.876(17)		
Bond angles (°)			
O(1)–Sm(1)–O(2)	126.2(2)	O(1)–Sm(1)–O(3)	98.1(2)
O(2)–Sm(1)–O(3)	76.9(2)	Sm(1)–O(1)–C(11)	161.2(4)
Sm(1)–O(2)–C(21)	161.6(4)	Sm(1)–O(2)–Li(1)	95.3(6)
C(21)–O(2)–Li(1)	102.5(7)	Sm(1)–O(3)–C(31)	158.7(5)
Sm(1)–O(3)–Li(1)	93.9(5)	C(31)–O(3)–Li(1)	103.4(6)
O(2)–Li(1)–O(3)	93.6(7)	O(2)–Li(1)–O(4)	134.4(10)
O(3)–Li(1)–O(4)	130.7(8)		

4. Experimental

4.1. General procedures and techniques

All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques, or under oxygen-free helium in a Vacuum Atmospheres glovebox. The compound 2,6-di-*tert*-butylphenol was purchased from Aldrich and used as received. The compound $KO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ was prepared following the reaction of a slight excess of potassium hydride (Aldrich) with 2,6-di-*tert*-butylphenol in THF. The compound LiC_5Me_5 was prepared from pentamethylcyclopentadiene and *n*-butyllithium in hexane. The compounds $Sm_2(OAr^*)_6$ and $Sm(OAr^*)_3(THF)_2$ were prepared as described previously ([7]b). Solvents were degassed and distilled from Na-benzophenone under nitrogen. Benzene-d_6 and toluene-d_8 were degassed, dried over an Na–K alloy and then trap-to-trap distilled before use. Methylene chloride-d_2 was trap-to-trap distilled from molecular sieves.

NMR spectra were recorded at 22°C on Brüker WM300 or Varian Unity 300 spectrometers. All ^1H-NMR chemical shifts are reported in ppm relative to the ^1H impurity in benzene-d_6, toluene-d_8 and methylene chloride-d_2 set at δ 7.15, 2.09 and 5.32 ppm, respectively. NMR spectra of paramagnetic lanthanide species are temperature dependent, thus it is important to note that the temperatures quoted represent average room temperatures (r.t.) and are approximate values. IR spectra were recorded on a Digilab FTS-40 spectrometer. Solid-state IR spectra were taken as Nujol mulls between KBr plates. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

4.1.1. $Sm(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(THF)$ (**1**)

Anhydrous $SmCl_3$ (1.00 g, 3.89 mmol) was suspended in THF (100 cm^3). To the vigorously stirred suspension was added solid $KO\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3$ (2.85 g, 11.66 mmol), resulting in an immediate change in color of the reaction mixture from white to yellow. The reaction mixture was allowed to stir overnight, and then all solvent was removed in vacuo. The resulting pale yellow solid was extracted with hexane (150 cm^3) and filtered through a Celite pad to give a clear yellow solution, which was then pumped to dryness to yield **1** as a yellow solid. Yield 0.900 g (28%). ^1H-NMR (300 MHz, C_6D_6): δ 8.24 (d, $J = 8$ Hz, 6H, *meta* OAr), 7.92 (t, $J = 8$ Hz, 3H, *para* OAr), 0.78 (s, 54H, $C(CH_3)_3$), -1.25 (v br, 4H, THF), -1.32 (br, 4H, THF). IR (Nujol, cm^{-1}); 1582 (w), 1407 (s), 1378 (s), 1366 (sh, m), 1352 (sh, m), 1316 (vw), 1260 (m), 1238 (s), 1213 (w), 1199 (m), 1151 (w), 1126 (w), 1120 (sh, w), 1103 (w), 1036 (vw), 1002 (m), 925 (vw), 915 (vw), 886, (w), 879 (w), 862 (s), 852 (sh, m), 831 (w), 820 (m), 799 (w), 752 (s), 667 (w), 654 (m), 590 (vw), 547 (w), 448 (w). Anal. Calc. for $C_{46}H_{71}SmO_4$: C, 65.89; H, 8.54; Found: C, 66.48; H, 8.01.

4.1.2. *(η-C_5Me_5)Sm(O-2,6-t-$Bu_2C_6H_3$)$_2$(THF)* (**2**)

To a yellow solution of Sm(O-2,6-*t*-$Bu_2C_6H_3$)$_3$(THF) (**1**) (0.364 g, 0.43 mmol) in THF (60 cm^3) was added solid LiC_5Me_5 (0.068 g, 0.48 mmol). The mixture was allowed to stir overnight during which time the solution appeared to deepen in color and a precipitate was observed. All solvent was removed in vacuo, and the pale yellow solid extracted into hexane (40 cm^3). Filtration through a Celite pad yielded a clear yellow solution which was concentrated to ca. 30 cm^3 and then allowed to evaporate in the glovebox atmosphere. Once the solvent had evaporated a yellow crystalline solid remained. This was rinsed with 2×10 cm^3 aliquots of $(Me_3Si)_2O$ and dried in vacuo. Yield 0.280 g (85%). ^{1}H-NMR (300 MHz, C_6D_6): δ 8.25 (d, $J = 8$ Hz, 4H, *meta* OAr), 7.93 (t, $J = 8$ Hz, 2H, *para* OAr), 1.68 (s, 15H, C_5Me_5), 0.75 (s, 36H, C(CH_3)$_3$), −1.05 (v br, 4H, THF), −2.65 (br, 4H, THF). Anal. Calc. for $C_{42}H_{65}O_3Sm(C_6H_{14})$ (hexane solvate): C, 67.47; H, 9.32; Found: C, 67.97; H, 8.92.

4.1.3. *[(η-C_5Me_5)Sm(OAr*)(μ-OAr*)$_2$Li(THF)]* (**4**) *(Ar* = 2,6-i-$Pr_2C_6H_3$)*

4.1.3.1. Method 1. To a solution of Sm_2(O-2,6-*i*-$Pr_2C_6H_3$)$_6$ (0.400 g, 0.29 mmol) in 80 cm^3 of THF was added solid LiC_5Me_5 (0.083 g, 0.58 mmol). The reaction mixture was allowed to stir at r.t. for 3 days, during which time the solution darkened to a deep yellow. Removal of solvent in vacuo left a yellow/orange oil which was extracted into hexane (100 cm^3) and filtered through a Celite pad. The filtrate was concentrated to 20 ml and placed at −40°C leading to the formation of a microcrystalline solid. The solid was redissolved in toluene (20 cm^3) and the solution allowed to slowly evaporate in the glovebox atmosphere. Once the solvent had evaporated, large yellow crystals with an oily coating were present. The crystals were rinsed with cold hexane and pumped dry. Yield 0.265 g (51%). ^{1}H-NMR spectroscopy of the desolvated material revealed the presence of a small amount of residual toluene and indicated the approximate formula [Cp*Sm(OAr*)$_3$Li(THF)] · $(C_7H_8)_{0.16}$. ^{1}H-NMR (300 MHz, C_6D_6): δ 7.12 (t, $J = 7$ Hz, 3H, *para* OAr), 6.98 (d, $J = 7$ Hz, 6H, *meta* OAr), 4.14 (br, 4H, α-THF), 1.75 (br, 4H, β-THF), 1.12 (s, 15H, C_5Me_5), 0.45 (v br, 6H, C*H*Me_2), −0.23 (br s, 36H, CH*Me*$_2$). IR (Nujol, cm^{-1}); 1589 (m), 1431(s), 1366 (sh, s), 1360 (sh, s), 1325 (s), 1271 (s), 1256 (s), 1204 (s), 1199 (s), 1156 (vw), 1142 (vw), 1105 (w), 1096 (w), 1057 (vw), 1040 (m), 1031 (m), 975 (vw), 952 (vw), 941 (vw), 934 (vw), 918 (vw), 894 (sh, w), 885 (m), 863 (m), 849 (sh, s), 844 (s), 804 (w), 797 (w), 756 (s), 743 (s), 728 (m), 693 (m), 686 (m), 598 (w), 560 (m), 556 (m), 524 (w). Anal. Calc. for $C_{50}H_{74}LiO_4Sm(C_7H_8)_{0.16}$: C, 67.38; H, 8.33. Found: C, 67.87; H 8.53.

4.1.3.2. Method 2. To a solution of Sm(O-2,6-*i*-$Pr_2C_6H_3$)$_3$(THF)$_2$ (1.28 g, 1.55 mmol) in THF (70 cm^3) was added LiC_5Me_5 (0.221 g, 1.55 mmol) as a solid. The mixture was allowed to stir overnight, during which time the solution had become orange in color. The solvent was removed in vacuo to leave an orange/yellow solid. The solid was extracted repeatedly with hexane (total 200 cm^3) and filtered through a Celite pad to give a clear yellow solution. The solution was pumped dry to yield a bright yellow solid. Yield 1.10 g (79%).

4.2. *[Li(TMEDA)$_2$][(η-C_5Me_5)Sm(OAr*)$_3$]* (**5**)

To a solution of **4** (0.327 g, 0.36 mmol) in hexane (70 cm^3) was added TMEDA (0.5 cm^3) dropwise. The initial yellow solution immediately decolorized and an off-white solid precipitated. The solution was allowed to stir for ca. 15 min, after which time the precipitate was allowed to settle and the mother liquor decanted off. The precipitate was washed with hexane (2×20 cm^3) and dried under reduced pressure to yield an almost white solid. Yield 0.200 g (53%). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 7.06 (d, $J = 8$ Hz, 6H, *meta* OAr), 6.85 (t, $J = 8$ Hz, 3H, *para* OAr), 2.83 (br, 6H, C*H*Me_2), 2.50 (br, 8H, CH_2CH_2), 2.32 (br s, 24H, NMe_2), 1.52 (s, 15H, C_5*Me*$_5$), 0.64 (d, $J = 7$ Hz, 36H, CH*Me*$_2$). IR (Nujol, cm^{-1}): 1586 (m), 1429 (s), 1367 (m), 1358 (m), 1344 (sh, m), 1334 (s) 1282 (sh, m), 1270 (s), 1246 (m), 1208 (m), 1181 (vw), 1159 (w), 1141 (vw), 1127 (w), 1109 (w), 1098 (w), 1068 (w), 1058 (w), 1041 (m), 1030 (m), 1012 (w), 974 (vw), 946 (m), 936 (sh, w), 887 (m), 857 (s), 804 (w), 788 (m), 774 (vw), 750 (s), 690 (m), 595 (vw), 563 (m), 554 (m). Calc. for $C_{58}H_{98}LiN_4O_3Sm$: C, 65.92; H, 9.35; N, 5.30. Found: C, 65.95; H 9.69; N, 5.19.

5. Crystallographic studies

5.1. *(η-C_5Me_5)Sm(O-2,6-t-$Bu_2C_6H_3$)$_2$(THF) · C_6H_{14}* (**2**)

A yellow, rectangular block measuring $0.57 \times 0.35 \times 0.35$ mm was mounted on a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, was then immediately placed under a nitrogen coldstream on an Enraf-Nonius CAD4 diffractometer. The radiation used was graphite monochromated Mo–K_α radiation ($\lambda =$

0.71073 Å). Unit cell parameters were determined from the least-squares refinement of $(\sin \theta/\lambda)^2$ values for 24 accurately centered reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections. The data were reduced using the Structure Determination Package provided by Enraf-Nonius and corrected for absorption empirically using high chi psi-scans. The intensities were corrected for Lorentz and polarization effects, equivalent reflections were merged ($R_{\mathrm{int}} = 0.041$) and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods, using full-matrix least-squares refinement. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to 'ride' upon the appropriate carbon atoms, final refinement using 4534 unique observed $[F > 4\sigma(F)]$ reflections converged at $R = 0.049$, $R_w = 0.063$ (where $w = [\sigma^2(F) + 0.0024(F)^2]^{-1}$). All data refinement calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instr., Inc, 1990).

5.2. $[(\eta\text{-}C_5Me_5)Sm(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_3Li(THF)] \cdot C_7H_8$ (4)

A yellow block measuring 0.53 × 0.34 × 0.32 mm was mounted on a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, was then immediately placed under a nitrogen coldstream on a Siemens R3m/V diffractometer. The radiation used was graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). The lattice parameters were optimized from a least-squares calculation on 50 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 1.30° scan range. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time, and three orientation controls were measured every 250 reflections.

The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans was applied. Equivalent reflections were merged ($R_{\mathrm{int}} = 0.019$) and systematically absent reflections were rejected. The structure was solved by routine Patterson and Fourier methods, using full-matrix least-squares refinement. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to 'ride' upon the appropriate carbon atoms, final refinement using 6503 unique observed $[F > 3\sigma(F)]$ reflections converged at $R = 0.080$, $R_w = 0.087$ (where $w = [\sigma^2(F) + 0.0002(F)^2]^{-1}$). All data refinement calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instr., Inc, 1990).

6. Supporting information

Listings of fractional atomic coordinates, bond lengths and angles, anisotropic thermal parameters and hydrogen atom coordinates for complexes **2** and **4** (20 pages) are available. Ordering information is given on any current masthead page.

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