Rare Earth Complexes of Bulky 2,6-Diphenylphenolates Containing Additional, Potentially Buttressing 3,5-Substituents[‡]

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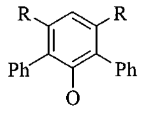
The rare earth aryloxide complexes, $[Yb(OAr^{tBu})_3(THF)]\cdot THF$, $[Sc(OAr^{tBu})_3(THF)]\cdot THF$, $[Yb(OAr^{Me})_3(THF)]$, and $[Sm(OAr^{Ph})_3(THF)_2]$ (OAr^R = 2,6-diphenyl-3,5-di-R-phenolate), have been prepared by redox transmetallation/ligand exchange between the rare earth metal, bis(pentafluorophenyl)mercury, and $HOAr^R$ in tetrahydrofuran. This reaction also provided $[Yb(OAr^{Ph})_3(DME)]\cdot 3/2THF$ by incorporation of adventitious 1,2-dimethoxyethane. A similar reaction between Yb metal, diphenylmercury, and $HOAr^{Me}$ gave $[Yb(OAr^{Me})_2(THF)_3]$. The homoleptic complexes $[Yb(OAr^{Ph})_3]$ and $[Sc(OAr^H)_3]$ have been prepared by direct reaction of the rare earth element with $HOAr^R$ in a sealed tube in the presence of mercury at elevated temperatures (200–250 °C) and the latter was converted into $[Sc(OAr^H)_3(THF)]$ by treatment with THF. X-ray crystal structure determinations of $[Yb(OAr^{tBu})_3(THF)]\cdot THF$, $[Sc(OAr^{tBu})_3(THF)]\cdot THF$, and $[Yb(OAr^{Me})_3(THF)]$ show the complexes to be monomeric and four coordinate with a trigonal pyramidal stereochemistry. These structures provide clear evidence that groups *meta* to the phenolate donor can modify the coordination behaviour of the 2,6-diphenylphenolate ligand. In $[Yb(OAr^{Ph})_3(DME)]\cdot 3/2THF$ a distorted square pyramidal stereochemistry is observed. The divalent complex $[Yb(OAr^{Me})_2(THF)_3]$ exhibits a distorted trigonal bipyramidal arrangement of the oxygen donor atoms with apical THF ligands. The homoleptic scandium 2,6-diphenylphenolate has three oxygen atoms in a triangular array with additional π-η^1-Ph···Sc interactions above and below the ScO_3 plane [C–Sc–C = 154.2(8)°], providing a new type of binding of this aryloxide ligand.

Introduction

Amongst rare earth aryloxides and alkoxides,[1] 2,6-di-*tert*-butyl-4-X-phenolates (X = H, Me, *t*Bu) have been seminal in stabilising low coordination numbers,[2] especially in homoleptic complexes.[2a−2c,2h,2i] With the less bulky[3a,3b] 2,6-diphenylphenolate, low coordination number complexes can still be obtained,[4] but the homoleptic lanthanoid(II or III) 2,6-di-phenylphenolates are noteworthy for intramolecular π-Ph···Ln interactions (η^1; η^2; η^3; η^4; η^6)[4a,4c,5] in addition to oxygen coordination, which can be quite irregular.[5a] One way of potentially increasing the bulkiness of 2,6-diphenylphenolate ligands[3b] is to add 3,5-substituents, which should reduce the flexibility of the phenyl groups and cause them to shield the donor atoms more. A range of such ligands is now available (e.g. **1b−c**) and exploration of their *d*-block and main group coordination chemistry has commenced.[6]



1a OAr^H, R = H
1b OAr^{Me}, R = Me
1c OAr^{tBu}, R = *t*Bu
1d OAr^{Ph}, R = Ph

We now examine the effect of buttressing substituents in rare earth chemistry with the synthesis and structural study of complexes with ligands **1b−1d**. In addition the homoleptic scandium complex with the parent ligand **1a** has been prepared and the structure determined. Previous studies of $[Ln(OAr^H)_3]$ complexes[5b] did not extend to the smaller (and much more expensive) Sc. It is of interest to determine the effect of reduced metal size on intramolecular π-Ph···Ln coordination, so far observed in $[Ln(OAr^H)_3]$ complexes as $\eta^6 + \eta^3$ (Ln = La) and $\eta^6 + \eta^1$ (Ln = Ce, Pr, Nd, Y, Yb, Lu).[4a,4c,5b]

Results and Discussion

Syntheses

Reaction of lanthanoid metals with bis(pentafluorophenyl)mercury, and 2,6-diphenyl-3,5-di-R-phenols **1b−1d** in tetrahydrofuran yielded the complexes $[Yb(OAr^R)_3THF]$

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(R = Me or *t*Bu), [Sm(OAr^{Ph})$_3$(THF)$_2$], and [Sc(OAr^{tBu})$_3$(THF)] [Equation (1)].

$$2\,\mathrm{Ln} + 3\,\mathrm{Hg(C_6F_5)_2} + 6\,\mathrm{HOAr^R} \longrightarrow 2\,\mathrm{Ln(OAr^R)_3} + 3\,\mathrm{Hg} + 6\,\mathrm{C_6F_5H} \tag{1}$$

From an analogous reaction with ytterbium metal and HOAr^{Ph}, the product was found to contain fortuitously incorporated DME, even though it was isolated as a THF solvate, [Yb(OAr^{Ph})$_3$(DME)]·1.5THF [Equation (1); R = Ph]. The complex was also obtained as a DME solvate from a similar reaction in DME, but could not be obtained pure (see Experimental Section). When diphenylmercury was used in place of Hg(C_6F_5)$_2$ in the reaction with HOAr^{Me}, the divalent complex [Yb(OAr^{Me})$_2$(THF)$_3$] was obtained [Equation (2)].

$$\mathrm{Yb} + \mathrm{HgPh_2} + 2\,\mathrm{HOAr^{Me}} \longrightarrow \mathrm{Yb(OAr^{Me})_2} + \mathrm{Hg} + 2\,\mathrm{PhH} \tag{2}$$

In previous redox transmetallation/ligand exchange reactions with Hg(C_6F_5)$_2$, Yb^{III} complexes have been obtained with HOAr^{H} [4a] whereas Yb^{II} derivatives have been isolated with 2,6-di-*tert*-butylphenolate ligands,[2d−2f] despite the general use of an excess of lanthanoid metal. However, in redox transmetallation/ligand exchange reactions of ytterbium with 3,5-di-*tert*-butylpyrazole, use of Hg(C_6F_5)$_2$ gave trivalent complexes[7] whereas HgPh$_2$ provided divalent compounds,[8] a relationship now seen with 2,6-diphenyl-3,5-dimethylphenol. Electrochemical studies[9] as well as synthetic behaviour[7,8,10] show that Hg(C_6F_5)$_2$ is a more powerful oxidant than HgPh$_2$.

The synthesis of homoleptic complexes was also attempted by direct reaction of metals with HOAr^R (R = Ph or *t*Bu) at elevated temperature in the presence of mercury. In general, decomposition products were obtained or the resulting lanthanoid complexes could not be crystallised, viz. from Yb/HOAr^{tBu} at 250 °C, Yb/HOAr^{Ph} at 300 °C and at 200−220 °C, and Nd/HOAr^{Ph} at 200−300 °C. However, reaction of Yb with HOAr^{Ph} strictly at 200 °C (i.e. below the ligand melting point) allowed [Yb(OAr^{Ph})$_3$] to be prepared in good yield [Equation (3), Ln = Yb, R = Ph].

$$\mathrm{Ln} + 3\,\mathrm{HOAr^R} \xrightarrow{\mathrm{Hg}} 3/2\,\mathrm{H_2} + \mathrm{Ln(OAr^R)_3} \tag{3}$$

This contrasts with the corresponding reaction of Yb with HOAr^H, which yields [Yb(OAr^H)$_2$]$_2$ and the mixed oxidation state complex [Yb$^{II}_2$(OAr^H)$_3$][Yb^{III}(OAr^H)$_4$].[5a] In addition, [Sc(OAr^H)$_3$] was obtained by reaction (3) (Ln = Sc, R = H), showing that for the 2,6-diphenylphenolate ligand, the method is applicable to the smallest rare earth metal. Crystallization from THF gave the solvate [Sc(OAr^H)$_3$(THF)].

Properties and Characterisation

Because of the difficulty in obtaining entirely satisfactory microanalyses for Ln(OAr^R)$_3$ (R = Me, *t*Bu, Ph), a feature previously noted for complexes of these buttressed ligands[6] and attributed to carbide formation,[6a] knowledge of the composition of the complexes is particularly dependent on X-ray structure determinations. These have been carried out for [Yb(OAr^{tBu})$_3$(THF)]·THF, [Yb(OAr^{Me})$_3$(THF)], [Sc(OAr^{tBu})$_3$(THF)]·THF, and [Yb(OAr^{Ph})$_3$(DME)]·1.5THF, as well as the analytically satisfactory [Yb(OAr^{Me})$_2$(THF)$_3$] and [Sc(OAr^H)$_3$] (next section). In contrast, complexes of the OAr^H ligand do not normally present analytical difficulties.[4,5] Microanalyses and metal analyses for bulk [Ln(OAr^{tBu})$_3$(THF)]·THF (Ln = Sc, Yb) and [Yb(OAr^{Me})$_3$(THF)] dried for 1−2 h under vacuum at room temperature, though somewhat divergent from calculated C values, suggested that these drying conditions did not remove coordinated THF or THF of solvation. This was supported by NMR integrations in the case of the scandium complex, although meaningful spectra could not be obtained for the paramagnetic Yb^{III} complexes. Both [Ln(OAr^{tBu})$_3$(THF)]·THF complexes have infrared absorptions at ca. 910 and 860 cm^{-1} plausibly attributable[10,11] to ring stretching of free (e.g. solvent of crystallisation) and coordinated THF, respectively. Tris(2,3,5,6-tetraphenylphenolato)samarium(III) was isolated with satisfactory analyses for a bis(THF) species. Since the sample was dried at 80 °C under vacuum, it is plausible that both ether molecules are coordinated, an effect of the larger size of Sm^{3+} than Yb^{3+}.[12] Aryloxide IR absorptions at 910−850 cm^{-1} (see [Yb(OAr^{Ph})$_3$]) rule out the use of IR spectroscopy to ascertain the nature of THF in the Sm complex. Single crystals of [Sc(OAr^H)$_3$(THF)] could not be grown, but it seems uncontentious that THF is coordinated in view of the structure of [Sc(OAr^{tBu})$_3$(THF)]·THF with a bulkier phenolate ligand, and since THF is retained on drying at 150 °C under vacuum. Moreover, the THF resonances are shifted from the "free" values consistent with coordination in solution (see Experimental Section). The analyses of the bulk sample of [Yb(OAr^{Ph})$_3$(DME)] dried at 80 °C are marginally closer for this composition than for [Yb(OAr^{Ph})$_3$(DME)]·1.5THF, which is the composition of the undried single crystals. An IR absorption at 1044 cm^{-1}, not observed for [Yb(OAr^{Ph})$_3$], is indicative of coordinated DME.[4d,13] A sample of the complex prepared in DME and dried at room temperature under vacuum was not obtained analytically pure but the analyses (especially for Yb) favoured the composition [Yb(OAr^{Ph})$_3$(DME)]·DME. The divalent complex [Yb(OAr^{Me})$_2$(THF)$_3$] gave satisfactory analyses and the ^{1}H NMR spectrum in C_6D_6 is consistent with this composition. However, the detection of two methyl resonances, a single, very broad THF resonance, and underlying broadness in the aromatic region suggests that an equilibrium occurs in C_6D_6 [Equation (4)] with both complexes detectable by their Me resonances.

$$[\mathrm{Yb(OAr^{Me})_2(THF)_3}] \rightleftharpoons [\mathrm{Yb(OAr^{Me})_2(THF)_2}] + \mathrm{THF} \tag{4}$$

Complexes of both compositions have been observed for the bulky 2,6-di-*tert*-butylphenolate ligands.[2e,2f,2i]

The mass spectra of several representative complexes were recorded. Surprisingly, ions with three OAr^R ligands were detected only for [Yb(OAr^{Me})$_3$(THF)]. In other cases, as well as for [Yb(OAr^{Me})$_2$(THF)$_3$], [Ln(OAr^R)$_2$]$^+$ was the highest structurally significant feature. Near infrared absorption at 900−1000 nm was observed for the Yb^{III} complexes, as expected,[14] but appropriately was absent for $[Yb(OAr^{Me})_2(THF)_3]$.

Molecular Structures

The Complexes $[Ln(OAr^{tBu})_3(THF)]\cdot THF$ (Ln = Yb or Sc) and $[Yb(OAr^{Me})_3(THF)]$

The structures of these complexes are closely related. Two representative structures in which the metal size and the aryloxide ligand are varied are shown in Figure 1 and 2, with Ln-based distances and angles in Table 1. All three complexes are four-coordinate monomers, displaying a stereochemistry substantially distorted from tetrahedral, similar to that of $[Yb(OC_6H_2tBu_3\text{-}2,4,6)_3(THF)]$.[2g] The striking reduction in coordination number from five in $[Yb(OAr^{H})_3(THF)_2]$,[4a] especially given the further THF present as solvent of crystallisation, indicates that OAr^{R} (R = *t*Bu, Me and presumably also Ph) ligands can be considered bulkier than the simple 2,6-diphenylphenolate, consistent with buttressing of the 2,6-diphenyl substituents by the 3,5-substituents. There are no unusual features in the packing of the 2,6-diphenyl substituents, which are common to the three compounds, and they do not appear to have any overriding influence on the stereochemistry. Thus the interplanar angles involving the phenyl substituents (Table 2) vary markedly between the three complexes. Some similarity is evident between the two complexes with OAr^{tBu} ligands, but there are still some significant differences (Table 2).

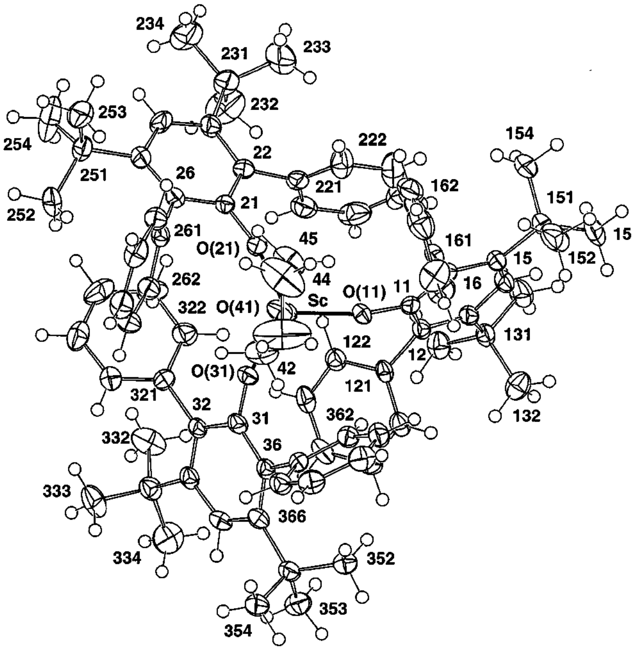

Figure 1. Molecular projection of $[Sc(OAr^{tBu})_3(THF)]$

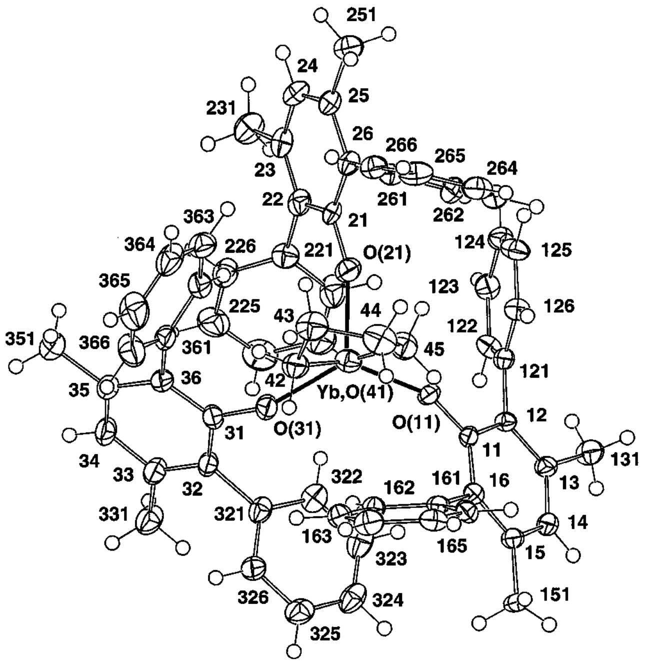

Figure 2. Molecular projection of $[Yb(OAr^{Me})_3(THF)]$

Table 1. Metal atom environments, $[Ln(OAr^{R})_3(THF)]$; the three values in each entry are for Ln/R = Sc/*t*Bu, Yb/Me and Yb/*t*Bu, respectively; in this and subsequent tables, *r* is the metal−ligand distance; other entries are the angles subtended at the metal by the relevant atoms at the head of the row and column

Atom	*r*	O(21)	O(31)	O(41)
O(11)	1.913(3) 2.032(4) 2.038(3)	111.5(1) 106.4(2) 111.8(1)	116.8(1) 121.7(1) 122.39(9)	106.4(1) 106.8(1) 104.3(1)
O(21)	1.914(3) 2.033(4) 2.029(3)		117.9(1) 117.6(1) 113.5(1)	100.6(1) 100.7(2) 99.34(9)
O(31)	1.922(3) 2.045(4) 2.042(3)			100.7(1) 100.7(2) 101.6(1)
O(41) (THF)	2.118(2) 2.247(4) 2.236(2)			

The Ln−OAr^{R} bond lengths (Table 1) show little variation for each compound and between the two $[Yb(OAr^{R})_3(THF)]$ (R = *t*Bu or Me) complexes. Subtraction of an extrapolated radius (from data in ref.[12]) for four coordinate Sc^{3+} or Yb^{3+} (0.62 and 0.75 Å, respectively) from $<Ln{-}OAr^{R}>$ gives 1.29−1.30 Å, which is within the usual range for bulky lanthanoid aryloxides, including $[Yb(OC_6H_2tBu_3\text{-}2,4,6)_3(THF)]$ (1.28 Å).[2g] However, the latter compound shows a wider variation in Ln−OAr bond lengths [1.97(1)−2.09(1) Å].[2g] There are similar Yb−O(THF) distances for the two Yb compounds, and subtraction of the four-coordinate ionic radius from Ln−O(THF) values gives 1.49−1.50 Å for the three $[Ln(OAr^{R})_3(THF)]$ complexes, at the low end of the range (1.49−1.59 Å) for THF complexes of bulky lanthanoid aryloxides.[2f,2g,4c,4d]

Table 2. Ligand descriptors (Å, degrees) for the complexes $[Ln(OAr^{R})_{n}(L)_{m}]$; θ values are dihedral angles between the C_6 ring planes [c: central; p2,6: peripheral; O_3: $O(n1)_3$]; δLn_c and δLnO_3 are the deviations of the metal atoms from the central and O_3 planes; R indicates the substituents at the 3- and 5-positions of the central ring; L (co-ligands if present) = THF or DME; Σ(O−Ln−O) is the sum of the angles defined by the phenolate oxygen atoms about the metal[a]

Ln/R	Sc/*t*Bu	Yb/Me	Yb/*t*Bu	Yb/Ph	Yb^{II}/Me	Sc/H
Ligand L_m	THF	THF	THF	DME	$(THF)_3$[a]	−
Ligand 1						
O(11)−C(11)	1.357(6)	1.347(6)	1.349(5)	1.35(1)	1.31(1)	1.38(3)
Ln−O(11)−C(11)	162.3(3)	157.0(3)	161.1(2)	170.3(6)	157.9(5)	144(2)
$\theta_{c/p2}$	74.6(2)	57.6(2)	74.5(1)	67.8(5)	56.4(3)	58.2(9)
$\theta_{c/p6}$	78.8(2)	67.7(2)	85.7(2)	71.4(5)	79.2(4)	57.4(10)
$\theta_{p2/p6}$	61.8(2)	82.2(2)	62.4(2)	60.2(6)	69.1(5)	56.6(9)
$\theta_{c/O3}$	66.2(1)	50.2(2)	64.7(1)	68.1(3)	−	83.6(8)
δLn_c	0.803(8)	0.77(1)	0.862(8)	0.40(2)	0.23(2)	0.02(3)
Ligand 2						
O(21)−C(21)	1.354(5)	1.342(6)	1.348(4)	1.34(1)	1.314(9)	1.38(3)
Ln−O(21)−C(21)	167.3(3)	163.0(3)	166.8(3)	161.8(7)	175.8(5)	144(2)
$\theta_{c/p2}$	80.8(2)	58.7(2)	86.6(2)	53.8(4)	47.1(5)	55.5(9)
$\theta_{c/p6}$	70.1(2)	68.9(2)	71.7(2)	54.5(4)	70.8(4)	56.0(9)
$\theta_{p2/p6}$	65.0(2)	49.4(2)	61.6(2)	88.9(4)	49.8(6)	57.1(9)
$\theta_{c/O3}$	45.6(1)	63.7(2)	46.5(1)	45.6(3)	−	79.4(8)
δLn_c	0.434(8)	0.57(1)	0.529(8)	0.06(2)	0.09(2)	0.27(5)
Ligand 3						
O(31)−C(31)	1.349(4)	1.341(6)	1.340(4)	1.35(1)		1.36(2)
Ln−O(31)−C(31)	157.6(3)	153.8(4)	154.5(3)	171.7(7)		178(2)
$\theta_{c/p2}$	70.1(2)	78.0(2)	71.9(2)	54.2(5)		45.0(10)
$\theta_{c/p6}$	74.0(2)	71.5(2)	74.3(1)	50.5(6)		43.7(10)
$\theta_{p2/p6}$	62.3(2)	64.1(2)	64.7(2)	57.7(6)		78.3(9)
$\theta_{c/O3}$	46.7(1)	47.8(2)	47.4(1)	34.0(3)		33.4(7)
δLn_c	0.887(8)	1.15(1)	1.026(7)	0.11(2)		0.12(6)
Σ(O−Ln−O)	$346._{2}$	$345._{7}$	$347._{7}$	$319._{6}$		$360._{0}$
δLnO_3	0.416(1)	0.448(1)	0.417(1)	0.772(1)		0.011(9)

[a] Dihedral angles of the second disordered component of substituent ring 6 to its associated central and other peripheral planes are 68.6(6), 49.8(6), and to its first component 2.8(5)°. In $[Yb(OAr^{Ph})_3(DME)]$, 3,5-substituent C_6 planes in the three ligands lie at 55.6(6), 55.3(5); 57.9(5), 52.7(4); 57.1(6), 49.5(5)° to their central C_6 planes.

There are significant variations of the O−Ln−O angles within each of the three structures (Table 1), indicating considerable distortion from tetrahedral stereochemistry. The sum of the $OAr^{R}-Ln-OAr^{R}$ angles in all three structures (Table 2) approaches 360°, whereas the sums of the $O(THF)-Ln-OAr^{R}$ angles are below the 328.5° expected for tetrahedral angles. Thus, the data suggest that four coordination in the three structures can be considered near *triangular pyramidal*. The Ln−O−C angles in the three structures are appreciably nonlinear (Table 2) and are comparable with the average ($156._{7}$°) found for the more crowded $[Yb(OC_6H_2tBu_3\text{-}2,4,6)_3(THF)]$.[2g] The deviation of the rare earth ions from the LnO_3 (aryloxide) plane (Table 2) is marginally more than 0.392(1) Å for $[Yb(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_3(THF)]$.[2g]

The Complex $[Yb(OAr^{Ph})_3(DME)]\cdot 1.5THF$

This complex has a five-coordinate array of three aryloxide and two DME oxygens (Figure 3). The best fit[15] polyhedron is a square pyramid (though very distorted) with O(11) as the apex, and *cisoid* aryloxides and DME in the base. It is thus very similar to the structures of $[Ln(OAr^{H})_3(DME)]$ (Ln = Yb or Nd).[4d] Thus, the 3,5-substituents do not affect the coordination number in contrast to complexation with THF (above). This is because a chelating DME has less steric demand than two THF ligands.[3a]

Since the $Ar^{Ph}O-Yb-OAr^{Ph}$ angles (Table 3) lie close to tetrahedral values (*cf.* Σ $ArO^{R}-Yb-OAr^{R}$, Table 2), there is an approximately tetrahedral array of aryloxide oxygens and the centre of the O···O vector of the DME. The *cisoid* aryloxide angle in the square plane [O(21)−Yb−O(31) 109.0(3)°] is surprisingly smaller than the corresponding *cisoid* angles in $[Ln(OAr^{H})(DME)]$ [Ln = Nd (120.3(2) and Yb (113.3(2)°].[4d] Although the O(DME)−Yb−O(DME) and the Yb−O(n1)−C(n1) (*n* = 1 and 2) angles are similar in the two complexes (R = H[4d] or Ph), the Yb−O(31)−C(31) angle in $[Yb(OAr^{Ph})_3(DME)]\cdot 1.5THF$ is $23._{4}$° greater (Table 3) than in $[Yb(OAr^{H})_3(DME)]\cdot 0.5DME$.[4d] Thus, the bond angles present no

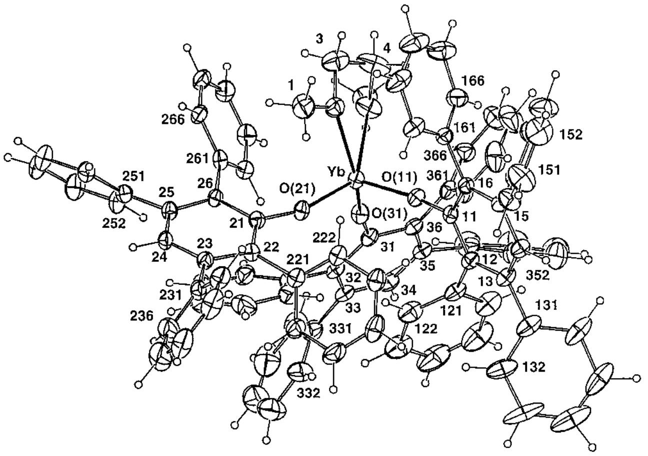

Figure 3. Molecular projection of [Yb(OAr^{Ph})$_3$(DME)]

Table 3. Ytterbium environment, [Yb(OAr^{Ph})$_3$(DME)]; O(2,5) from DME[a]

Atom	r	O(21)	O(31)	O(2)	O(5)
O(11)	2.038(7)	101.8(3)	108.8(3)	97.3(3)	111.2(3)
O(21)	2.048(7)		109.0(3)	84.1(3)	137.4(3)
O(31)	2.043(8)			146.9(3)	85.3(3)
O(2)	2.379(9)				66.1(3)
O(5)	2.349(9)				

[a] Torsions in the DME ring (only bonds specified): Yb−O(2,5) 5.6(9), 22(1); O(2)−C(3) −28(1); O(5)−C(4) −48(2); C(3)−C(4) 48(2); O(5)−Yb−O(2)−C(1) 161(1); O(2)−Yb−O(5)−C(6) −147(1)°.

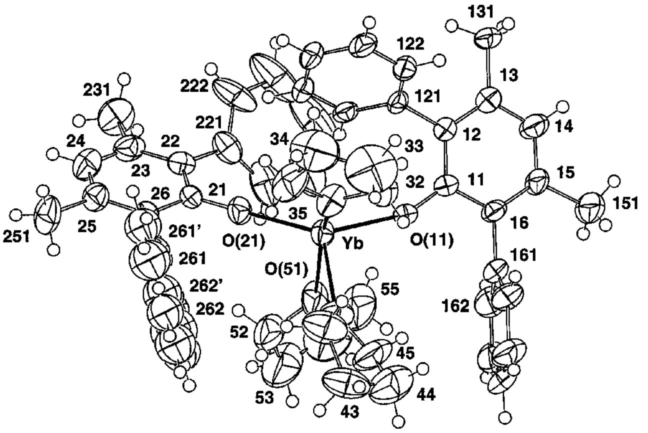

Figure 4. Molecular projection of [Yb(OAr^{Me})$_2$(THF)$_3$]

Table 4. Ytterbium environment, [Yb(OAr^{Me})$_2$(THF)$_3$]; O(31)−O(51) are derivatives of the THF ligands

Atom	r	O(21)	O(31)	O(41)	O(51)
O(11)	2.218(6)	140.9(2)	95.8(2)	100.7(2)	91.1(2)
O(21)	2.202(6)		100.7(2)	117.1(2)	87.6(2)
O(31)	2.397(6)			78.7(2)	156.7(3)
O(41)	2.426(6)				78.1(3)
O(51)	2.436(7)				
C(126)	3.177(9)				

clear picture as to the effect of 3,5-disubstitution on DME complexation. The <Yb−OAr> and <Yb−O(DME)> distances of [Yb(OAr^{Ph})$_3$(DME)]·1.5THF correspond closely to those of [Yb(OAr^{H})$_3$(DME)]·0.5DME (0.02, 0.03 Å difference).[4d]

The Complex [Yb(OAr^{Me})$_2$(THF)$_3$]

There is a five coordinate Yb^{II} centre in [Yb(OAr^{Me})$_2$(THF)$_3$] (Figure 4), and the best fit polyhedron[15] of the donor atoms is a trigonal bipyramid with the THF oxygens O(31) and O(51) apical and the aryloxide oxygens and O(41) (THF) equatorial. The stereochemistry is severely distorted with a 156.7(3)° angle between the axial donors and considerable variation [100.7(2)−140.9(2)°] (Table 4) in the equatorial angles, though their sum is 358.$_7$°.

There is also a close approach of a carbon atom [Yb···C(126) = 3.177(9) Å] adjudged just on or outside the limit for meaningful binding. If viewed as six coordinate, subtraction of the appropriate Yb^{2+} ionic radius[12] from the Yb···C distance gives 2.16 Å, which is the upper limit for significant intramolecular π-C(Ph)···Ln interactions,[16] whereas subtraction of the extrapolated five coordinate radius gives 2.22 Å, beyond the range. The calculated position of H(126) is even closer to Yb [2.9(est.) Å] and intrudes into and can explain the large [140.9(2)°] O(11)−Yb−O(21) angle without postulation of an Yb···H interaction. Certainly, the large angle cannot be explained by repulsion between the bulky aryloxide ligands as *cisoid* Ar^{R}O−Yb−OAr^{R} angles are well established, for example in [Yb(OAr^{Ph})$_3$(DME)] (Table 3). Although [Yb(OAr^{H})$_2$(THF)$_3$] is also distorted trigonal bipyramidal, the aryloxide ligands are apical [Ar^{H}O−Yb−OAr^{H} = 164.6(3)°] with highly distorted angles between the equatorial THF ligands [O−Yb−O = 83.7(4), 138.8(3), 137.5(3)°].[4d] In this case, aryl hydrogens intrude into both of the large O(THF)−Yb−O(THF) angles, though at greater distances [Yb···H = 3.1, 3.2 Å; nearest associated C at 3.45(1) Å] than for [Yb(OAr^{Me})$_2$(THF)$_3$].

The average Yb−OAr distance (2.21 Å) is in agreement with those (2.21−2.22 Å) of [Yb(OAr^{H})$_2$(THF)$_3$][4d] and square pyramidal [Yb(OC$_6$H$_2$*t*Bu$_2$-2,6-X-4)$_2$(THF)$_3$]. THF (X = Me, *t*Bu).[2e,2f] Whilst <Yb−O(THF)> (2.42 Å) agrees with that of [Yb(OAr^{H})$_2$(THF)$_3$],[4d] it is shorter than those (2.48, 2.46 Å) of the two 2,6-di-*tert*-butylphenolate complexes.[2e,2f] Subtraction of the ionic radius for five coordinate Yb^{2+} gives 1.46 Å, rather lower than the usual range 1.48−1.60 Å for THF in bulky aryloxide complexes of Yb^{II}/Yb^{III}.[2f,2g,4a,4d] (It would be even lower if Yb^{II} were to be taken as six coordinate). Despite the similarity in <Yb−O(THF)> values between [Yb(OAr^{R})$_2$(THF)$_3$] (R = H[4d] or Me) derivatives, the present complex shows a much smaller range of lengths (0.03$_9$ Å) than the earlier complex (0.1$_5$ Å).[4d] The Yb−OAr^{R}−C angles are similar in the two structures (Table 2 and ref.[4d]) despite the different arrangement of ligands.

[Sc(OAr)$_3$]

Single crystals of homoleptic [Yb(OAr^{Ph})$_3$] could not be obtained and hence the effect of 3,5-disubstitution on the structure of homoleptic lanthanoid 2,6-diphenylphenolates could not be determined. However, the complex [Sc(OAr^H)$_3$] has been shown to be monomeric (Figure 5), with the coordination sphere comprising a triangular array of phenolate oxygens and capping π-η^1-Ph···Sc interactions above and below the ScO$_3$ plane (see below). Unlike [Ce(OC$_6$H$_3$*t*Bu$_2$-2,6)$_3$][2b] and [Ln(OAr^H)$_3$] (Ln = Y, La, Ce, Nd, Pr, Yb, Lu)[4a,4c,5b] complexes, in which the LnO$_3$ units are distorted from triangular planar towards trigonal pyramidal, [Sc(OAr^H)$_3$] is triangular planar (O−Sc−O deviation from 120°: ≤ 2.3°; Σ O−Sc−O 360°) with minimal deviation of Sc from the O$_3$ plane (Table 2), much like [Ln(OC$_6$H$_2$*t*Bu$_2$-2,6-Me-4)$_3$] (Ln = Sc, Y).[2a,2c] The <Sc−O> distance is 1.93 Å and is somewhat longer than that of [Sc(OC$_6$H$_2$*t*Bu$_2$-2,6-Me-4)$_3$][2a] (1.87 Å), presumably owing to the higher coordination number of Sc in [Sc(OAr^H)$_3$] due to the C···Sc interactions.

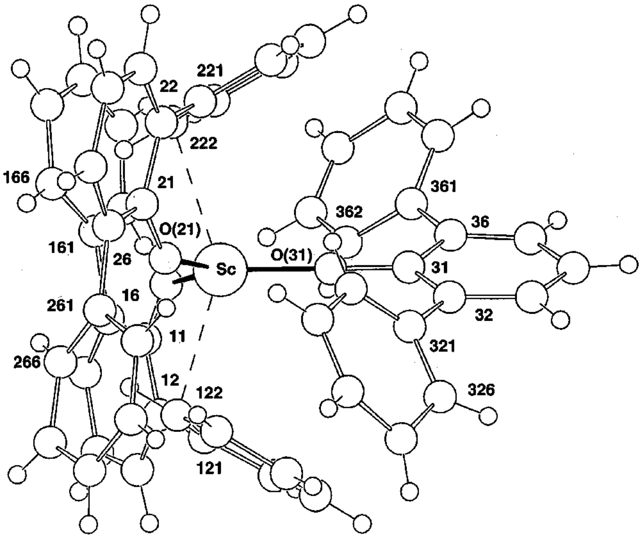

Figure 5. Molecular projection of [Sc(OAr^H)$_3$]

The phenyl rings 12n and 22n approach the ScO$_3$ plane from above and below such that C(122) and C(222) are closer to Sc than the next nearest C atoms of the rings by ca. 0.45 Å (Table 5). The Sc···C(122) and Sc···C(222) distances (Table 5) are not greatly lengthened from the π-η^1-Cp−Sc bridging bonds [2.629(4), 2.519(4) Å] of [ScCp$_3$]$_n$,[17] for which the next closest contacts from the η^1-bonded rings are more distant by ca. 0.4−0.6 Å. Subtraction of an extrapolated (from data of ref.[12]) radius (0.68 Å) for five coordinate Sc^{3+} from Sc···C of [Sc(OAr^H)$_3$] gives 1.94 and 2.00 Å, well within the upper limit (2.16 Å) for significant intramolecular π-Ph···Ln interactions.[16] Accordingly, C(122) and C(222) are considered to be weakly bound to Sc by π-η^1-Ph···Sc interactions. Even subtraction of a three coordinate Sc^{3+} radius from Sc···C(122) gives values within the 2.16 Å limit. With two π-η^1-Ph···Sc interactions, the capping phenyls have a different coordination mode than in [Ln(OAr^H)$_3$] (Ln = Ce, Pr, Nd, Y, Yb, Lu) (η^6 + η^1)[4a,4c,5b] or [La(OAr^H)$_3$] (η^6 + η^3),[5b] attributable to the small size of Sc^{3+}.[12] The similar Sc···C binding modes and bond lengths *transoid* to the O$_3$ plane probably account for the triangular ScO$_3$ arrangement and minimal deviation [0.011(9) Å] of Sc from the O$_3$ plane {cf. [Ln(OAr^H)$_3$]: 0.150(1)−0.353(1) Å (La−Lu)}.[4a,4c,5b] Although the *transoid* C(122)−Sc−C(222) angle [145.2(8)°] deviates considerably from linear, the ring centroids are nearer linear [C(120)−Sc−C(220) = $165._7$°]), although still less than the range $173._2$−$177._2$° for the other structurally characterised [Ln(OAr^H)$_3$] complexes.[4a,4c,5b] The inclinations of the capping phenyl rings 12n and 22n to the ScO$_3$ plane [30.8(8)°, 28.9(8)° Table 5] are similar to those [28.1(2)−30.1°] of the π-η^1-Ph···Ln bonded rings of [Ln(OAr^H)$_3$] (Ln = Ce, Pr, Nd, Yb, Lu).[4a,4c,5b] On the other hand, the rings are inclined to each other at 59.2(6)°, quite different from the dihedral angle of the η^6 and η^3 rings of [La(OAr^H)$_3$] [19.9(3)°] or of the η^6 and η^1 rings of [Lu(OAr^H)$_3$] [38.8(3)°].[5b]

Table 5. Scandium environment, [Sc(OAr^H)$_3$]

Atom	*r*	O(21)	O(31)	C(122)	C(222)
O(11)	1.92(2)	122.1(7)	117.7(7)	77.8(8)	86.0(8)
O(21)	1.97(2)		120.2(7)	84.7(8)	78.2(8)
O(31)	1.91(1)			107.2(9)	107.5(9)
C(122)	2.62(3)[a]				145.2(8)
C(222)	2.68(3)[a]				

[a] Next closest Sc···C contacts: Sc···C(121, 123; 221, 223) are 3.12(3), 3.08(3); 3.12(3), 3.19(3) Å. Planes 12n, 22n lie at 30.8(8), 28.9(8) to the O$_3$ plane and 59.2(6)° to each other; Sc lies 2.56(2) and 2.63(2) Å out of them.

Further examination of the [Sc(OAr^H)$_3$] structure shows that the Sc−O(11)−C(11) and Sc−O(21)−C(21) angles (ligands 1 and 2) are much smaller than 180° while Sc−O(31)−C(31) is nearly linear (Table 2). Furthermore, the dihedral angles (Table 2) between the C$_6$ central (phenolate) plane and the O$_3$ plane (θ$_c$/O$_3$) are 83.6(8) and 79.4(8)° for ligands 1 and 2 respectively, whilst only 33.4(7)° for ligand 3 (Table 2). Moreover, the angles between the central C$_6$ ring and the phenyl substituent planes of ligands 1 and 2 average $57._8$ and $55._8$°, whilst the average value for ligand 3 is 44.4°. The interplanar angles between the 2- and 6-phenyl rings for ligands 1 and 2 also differ from that of ligand 3 (Table 2). These data, in conjunction with the substantial bending of the Sc−O−C angles of ligands 1 and 2, demonstrate the deviation of ligands 1 and 2 towards Sc associated with binding of their phenyl substituents.

Conclusions

The reduction in coordination number from five in [Yb(OAr^H)$_3$(THF)$_2$][4a] to four in [Yb(OAr^R)$_3$(THF)] (R =

*t*Bu or Me) (see Figure 2) indicates that the addition of 3,5-substituents to the 2,6-diphenylphenolate ligand is consistent with an increase in ligand bulk, possibly by buttressing the phenyl groups. This reduction in coordination number is foreshadowed by the anomalous "4.5 coordination" in [Ln(OAr^{H})$_3$(THF)$_2$] (Ln = La and Nd).[4b,4c] In contrast, similar five coordinate structures are observed in [Yb(OAr^{R})$_3$(DME)] [R = H[4d] or Ph (Figure 3)]. In five coordinate [Yb(OAr^{R})$_2$(THF)$_3$], there is a change from apical aryloxides (R = H)[4d] to (surprisingly) apical THF ligands (R = Me) (Figure 4) in their distorted trigonal bipyramidal stereochemistry. In homoleptic [Sc(OAr^{H})$_3$], the coordination motif, ScO$_3$ + two π-η^1-Ph···Sc interactions, is new and differs from the ligation in other [Ln(OAr^{H})$_3$] complexes.[4a][4c][5b]

Experimental Section

General: Rare earth aryloxides are extremely air- and water-sensitive hence all operations were carried out under an inert atmosphere (purified Ar or N$_2$). Handling methods, analytical procedures, and solvent purifications were generally as described previously,[5b,18] with the exception of some infra red spectra and the ^{1}H NMR spectrum of [Yb(OAr^{Me})$_2$(THF)$_3$] which were recorded using a Perkin−Elmer Spectrum 2000 FTIR and a Varian Associates Gemini-200 spectrometer, respectively. IR data (4000−650 cm^{-1}) are for compounds as Nujol mulls. ^{1}H chemical shifts are referenced to internal solvent resonances and reported relative to SiMe$_4$. In assignments of ^{1}H NMR spectra involving the OAr^{H} ligand, primed numbers refer to phenyl protons. In the mass spectra, each listed *m*/*z* value for metal-containing ions (where the metal has more than one isotope) is the most intense peak of a cluster with an isotope pattern in good agreement with the calculated pattern. Those complexes containing OAr^{R} (R = *t*Bu, Ph) ligands for which data are not reported did not display any metal-containing ions in their mass spectra. Microanalyses were either by the Campbell Microanalytical Service, University of Otago, New Zealand or by Microanalytical services, Department of Chemistry at Purdue University, Indiana, USA. Complexes with THF or DME lose solvent on being heated in sealed capillaries under N$_2$ hence melting points have little significance (see examples below). 2,6-Diphenylphenol was purchased from Aldrich, while HOAr^{R} reagents were prepared by previously reported procedures (R = Me,[6b,19] *t*Bu,[20] Ph[21]). Rare earth metals were obtained as powders or chunks from Rhône−Poulenc, Phoenix, USA.

Tris(2,6-diphenyl-3,5-di-*tert*-butylphenolato)tetrahydrofuranytterbium(III)-Tetrahydrofuran (1/1): A 100 mL Schlenk flask was charged with ytterbium powder (0.52 g, 3.01 mmol), bis(pentafluorophenyl)mercury(II) (1.07 g, 2.00 mmol), 2,6-diphenyl-3,5-di-*tert*-butylphenol (1.43 g, 3.99 mmol) and THF (50 mL). The reaction mixture was stirred for 10 h at 80 °C yielding a dark red-brown solution upon filtration. The volume of the solution was reduced to 15 mL and yellow prismatic *single crystals* formed overnight which were used for X-ray crystal structure determination. More yellow crystals formed on storing the saturated solution at ambient temperature for several days. These were dried under vacuum at room temperature (0.75 g, 40%). − IR: $\tilde{\nu}$ = 1597w, 1576w, 1525w, 1296s, 1239w, 1171w, 1069m, 1027m, 1011m, 998s, 851w, 818w, 780w, 760m, 707s cm^{-1}. − Vis/near IR (THF): λ_{max} (ε) = 395 (52), 758 (25), 912 (3), 979 (10) nm (dm^3 mol^{-1} cm^{-1}). − $C_{82}H_{95}O_4Yb$ [Yb(OAr^{tBu})$_3$(THF)] (1317.62): calcd. C 74.74, H 7.27, Yb 13.13. − $C_{86}H_{103}O_5Yb$ (title compound) (1389.72): calcd. C 74.32, H 7.47, Yb 12.45; found C 73.36, H 7.44, Yb 11.33.

Tris(2,6-diphenyl-3,5-dimethylphenolato)(tetrahydrofuran)ytterbium(III): A mixture of 2,6-diphenyl-3,5-dimethylphenol (0.82 g, 3.00 mmol), bis(pentafluorophenyl)mercury(II) (0.80 g, 1.50 mmol) and ytterbium chips (0.52 g, 3.01 mmol) was stirred in THF (60 mL) at ambient temperature for 21 h. Filtration gave a bright yellow solution, which was partially evaporated and a small volume of hexane (10 mL) added. Large yellow crystals formed which were used for X-ray structure determination. The solution was then further reduced in volume producing more crystalline material which was dried under vacuum at room temperature (combined yield 0.43 g, 40%). − M.p. (sealed tube/N$_2$): 228−231 °C, prelim. dec. 80−90 °C. − IR: $\tilde{\nu}$ = 1598m, 1572w, 1554m, 1323s, 1169w, 1152w, 1089s, 1067m, 1027m, 1009m, 967m, 912w, 862m, 836m, 785w, 749s, 704s, 664s cm^{-1}. − Vis/near IR (THF): λ_{max} (ε) = 372 (364), 911 (14), 980 (50) nm (dm^3 mol $^{-1}$ cm^{-1}). − MS (70 eV, EI): *m*/*z* (%) = 994 (37) [Yb(OAr^{Me})$_3$ + H]$^+$, 979 (2) [Yb(OAr^{Me})$_3$ − CH$_2$]$^+$, 720 (100) [Yb(OAr^{Me})$_2$]$^+$, 705 (2) [Yb(OAr^{Me})$_2$ − Me]$^+$, 447 (18) [Yb(OAr^{Me})]$^+$, 428 (2) [Yb(OAr^{Me}) − MeH − 3H]$^+$, 371 (3) [Yb(OAr^{Me}) − C$_6$H$_4$]$^+$, 274 (28) [ArO^{Me}H]$^+$, 273 (35) [ArO^{Me}]$^+$. − $C_{64}H_{59}O_4Yb$ (1065.15): calcd. C 72.16, H 5.58, Yb 16.25; found C 70.08, H 5.67, Yb 15.64.

Tris(2,6-diphenyl-3,5-di-*tert*-butylphenolato)(tetrahydrofuran)-scandium(III) -Tetrahydrofuran (1/1): A mixture of 2,6-diphenyl-3,5-di-*tert*-butylphenol (1.08 g, 3.01 mmol), bis(pentafluorophenyl)mercury(II) (0.80 g, 1.50 mmol), small scandium chunks (0.36 g, 8.01 mmol) and mercury (2 drops) in THF (50 mL) was ultrasonicated at ambient temperature for 227 h. The reaction mixture was filtered through a Celite pad, giving a clear very pale yellow solution which was evaporated to 10 mL. Small colourless crystals appeared in a few hours, and these were used for X-ray crystallography. Bulk crystalline solid deposited from the decanted mother liquor on further standing, and was dried under vacuum at room temperature. More solid crystallised from the filtrate and was similarly treated (combined yield 0.57 g, 45%). − M.p. (sealed tube/N$_2$): 203−205 °C (dec.), prelim. dec. ca. 150 °C − IR: $\tilde{\nu}$ = 1597m, 1576m, 1522m, 1288s, 1238m, 1200m, 1171m, 1070m, 1027m, 1012s, 998s, 912m, 870m, 819w 780w, 761m, 708s, 658s cm^{-1}. − ^{1}H NMR (C$_6$D$_6$): δ = 1.28 (s, 54 H, *t*Bu), 1.41 [br s, 8 H, β-H(THF)], 3.56 [br s, 8 H, α-H(thf)], 6.88−7.58 (m, 33 H, ArH). − MS (70 eV, EI): *m*/*z* (%) = 759 (1) [Sc(OAr^{tBu})$_2$]$^+$, 743 (3) [Sc(OAr^{tBu})$_2$ − MeH]$^+$, 727 (1) [Sc(OAr^{tBu})$_2$ − 2MeH]$^+$, 711 (<1) [Sc(OAr^{tBu})$_2$ − 3MeH]$^+$, 671 (<1) [Sc(OAr^{tBu})$_2$ − MeH − Me − Bu]$^+$, 655 (<1) [Sc(OAr^{tBu})$_2$ − 2 MeH − Me − Bu]$^+$, 641 (<1) [Sc(OAr^{tBu})$_2$ − 3Me − MeH − Bu]$^+$, 358 (55) [Ar^{tBu}OH]$^+$, 57 (100) [Bu]$^+$. − $C_{86}H_{103}O_5Sc$, (1262.64): calcd. C 81.87, H 8.23, Sc 3.56; found C 80.89, H 8.26, Sc 4.13.

Tris(2,3,5,6-tetraphenylphenolato)bis(tetrahydrofuran)samarium(III): A mixture of 2,3,5,6-tetraphenylphenol, (1.32 g, 3.31 mmol), bis(pentafluorophenyl)mercury(II) (0.89 g, 1.66 mmol) and samarium powder (1.00 g, 6.65 mmol) was stirred in THF (40 mL) at room temperature for 29 h. Filtration gave a pale yellow solution which was evaporated to 10 mL. Pale yellow crystals formed in a few hours. The solid was dried under vacuum at 80 °C for 1 h giving a colourless-pale yellow powder (0.89 g, 54%). − IR: $\tilde{\nu}$ = 1597m, 1577w, 1531w, 1341s, 1307s, 1274m, 1138s, 1068m, 1025m, 1010m, 946s, 908w, 859w, 792w, 757s, 698s, 668s cm^{-1}. − ^{1}H NMR (C$_7$D$_8$): δ = −0.05 [br s, 8 H, β-H(THF)], 0.85 [br s, 8 H, α-H(THF)], 6.26−7.61 (complex m, 63 H, ArH). − $C_{94}H_{71}O_4Sm$ [Sm(OAr^{Ph})$_3$(THF)] (1414.91): C 79.79, H 5.05, Sm 10.63. −

$C_{98}H_{79}O_5Sm$ (1487.01): calcd. C 79.15, H 5.36, Sm 10.11; found C 78.32, H 5.44, Sm 10.02.

Adventitious Synthesis of Tris(2,3,5,6-tetraphenylphenolato)(1,2-dimethoxyethane)ytterbium(III): A mixture of 2,3,5,6-tetraphenylphenol, (1.59 g, 3.99 mmol), bis(pentafluorophenyl)mercury(II) (1.07 g, 2.00 mmol) and ytterbium powder (0.35 g, 2.02 mmol) was stirred in THF (50 mL) at 80 °C for 5 h. Filtration gave a dark red-brown solution which was evaporated to 20 mL and kept at −20 °C for 2 h. A very fine yellow crystalline solid, and later orange-yellow powder formed. This was dissolved in a minimal volume of hot toluene which was contaminated with a substantial amount of 1,2-dimethoxyethane. Meanwhile more crude product was obtained from the original THF solution. This was dissolved in hot toluene and the two toluene solutions were combined and left to stand at room temperature for several days resulting in initial formation of a large yellow crystal, which was cut in three and used for X-ray crystal structure identification as $[Yb(OAr^{Ph})_3(DME)]\cdot1.5THF$, and then bulk yellow microcrystalline product which was dried under vacuum at 80 °C for 1 h. More microcrystalline yellow product deposited from the filtrate, and was collected and dried as before {combined yield 0.31 g, 16% for $[Yb(OAr^{Ph})_3(DME)]$}. − IR: $\tilde{\nu}$ = 1597m, 1578w, 1530m, 1345s, 1306m, 1275m, 1142s, 1091w, 1071w, 1044m, 1001w, 994w, 952s, 908w, 870w, 846w, 793w, 758s, 698s, 871s cm^{-1}. − Vis/near IR (THF): λ_{max} (ε) = 399 (161), 912 (7), 980 (43) nm ($dm^3\ mol^{-1}\ cm^{-1}$). − $C_{100}H_{85}O_{6.5}Yb$ ($[Yb(OAr^{Ph})_3(DME)]\cdot1.5THF$) (1563.72): calcd. C 76.80, H 5.48, Yb 11.07. − $C_{94}H_{73}O_5Yb$ (THF-free) (1455.56): calcd. C 77.56, H 5.06, Yb 11.89; found C 78.72, H 5.44, Yb 11.43.

Bis(2,6-diphenyl-3,5-dimethylphenolato)tris(tetrahydrofuran)ytterbium(II): A mixture of 2,6-diphenyl-3,5-dimethylphenol (1.10 g, 4.01 mmol), diphenylmercury(II) (0.71 g, 2.00 mmol), ytterbium chips (0.69 g, 3.99 mmol) and mercury (2 drops) was stirred in THF at 50 °C for 29 h. Filtration gave a dark red-brown solution, which was evaporated to 5 mL and layered with hexane yielding a dark red crystalline product from which single crystals for X-ray structure determination were derived. The remaining bulk crystalline material was dried under vacuum at ambient temperature (0.83 g, 44%). − IR: $\tilde{\nu}$ = 1598m, 1551m, 1325s, 1296s, 1239w, 1153w, 1089s, 1068s, 966w, 916m, 879w, 788w, 750m, 704s cm^{-1}. − Vis/near IR (THF): no absorptions occurred near 1000 nm. − ^1H NMR (C_6D_6): δ = 0.90 (s, 6 H, CH_3), 1.25 (s, 6 H, CH_3), 2.04 [br s, 24 H, CH_2 (THF)], 6.63−7.08 (m, 22 H, ArH). Integrations are approximate owing to the broadness of the THF peak, the complexity and underlying broadness of the aromatic resonances, and the proximity of strong solvent absorptions to the aromatic resonances. − MS (70 eV, EI): *m*/*z* (%) = 720 (13) $[Yb(OAr^{Me})_2]^+$, 447 (3) $[Yb(OAr^{Me})]^+$, 274 (100) $[ArO^{Me}H]^+$. Additional clusters centred on *m*/*z* = 795, 748, and 733 of very low intensity (<1%) did not have a recognizable isotope pattern and could not be assigned. − $C_{52}H_{58}O_5Yb$ (936.02): calcd. C 66.72, H 6.25, Yb 18.49; found C 66.38, H 6.02, Yb 18.70.

Tris(2,3,5,6-tetraphenylphenolato)ytterbium(III): A mixture of ytterbium chips (0.52 g, 3.01 mmol) and 2,3,5,6-tetraphenylphenol (0.60 g, 1.51 mmol) was heated at 200 °C in the presence of mercury (2 drops) in a sealed tube under vacuum for 24 h. The reaction mixture was extracted in hot toluene (70 mL) and filtered giving an orange solution. The volume of the solution was reduced to 2 mL and pentane was layered on top. A microcrystalline yellow solid formed overnight. This was isolated, washed with hexane (2 mL) and dried at 60 °C under vacuum (0.52 g, 76%). − M.p. (sealed tube/N_2): 282−285 °C. − IR: $\tilde{\nu}$ = 1597w, 1581w, 1574w, 1531w, 1513w, 1347s, 1307m, 1276m, 1140m, 1070w, 1027w, 1010w, 949m, 908w, 873, 863, and 855vw, 800w, 775w, 758s, 722m, 698s, 672m cm^{-1}. − Vis/near IR (THF): λ_{max} (ε) = 348 (1634), 913 (8), 980 (40) nm ($dm^3\ mol^{-1}\ cm^{-1}$). − $C_{90}H_{63}O_3Yb$ (1365.44): calcd. C 79.16, H 4.65, Yb 12.67; found C 79.51, H 4.89, Yb 12.12.

Tris(2,6-diphenylphenolato)scandium(III): A mixture of scandium chips (0.36 g, 8.01 mmol) and 2,6-diphenylphenol (0.99 g, 4.02 mmol) was heated in the presence of mercury (2 drops) in a sealed Carius tube at 200−250 °C for 160 h. The reaction mixture was worked up in toluene (70 mL) and filtered while hot giving a colourless solution, which was evaporated to 5 mL. Some colourless single crystals formed overnight which were used for an X-ray crystal structure determination. Further standing gave a colourless microcrystalline solid which was isolated and dried at 80 °C for 1 h (0.44 g, 42%). − M.p. >220 °C. − IR: $\tilde{\nu}$ = 1579m, 1411s, 1307m, 1282s, 1248s, 1172m, 1162w, 1154w, 1112w, 1094w, 1068m, 1026w, 1010w, 990w, 970w, 890s, 867s, 804w, 763s, 702s, 634s, 610s cm^{-1}. − ^1H NMR (C_6D_6): δ = 6.86−6.96 (m, 21 H, H4, H3′, H4′, H5′), 7.19 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 6 H, H3, H5), 7.31 (dd, $^3J_{H\text{-}H}$ = 7.0 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, 12 H, H2′, H6′). − MS (70 eV, EI): *m*/*z* (%) = 535 (21) $[Sc(OAr^H)_2]^+$, 246 (100) $[HOAr^H]^+$. − $C_{54}H_{39}O_3Sc$ (780.81): calcd. C 83.06, H 5.03, Sc 5.76; found C 82.88, H 5.19, Sc 5.65.

Tris(2,6-diphenylphenolato)(tetrahydrofuran)scandium(III): Tris(2,6-diphenylphenolato)scandium was prepared as above and on the same scale, but THF (90 mL) was used rather than toluene to work up the reaction mixture. Filtration gave a colourless solution, which was evaporated to 2 mL, but no solid formed. THF was then removed completely leaving a white solid. Crystallisation from toluene (20 mL) gave a white microcrystalline solid, which was dried under vacuum at 150 °C for 1 h (0.72 g, 63%). − M.p. (sealed tube/N_2): 218−220 °C, prelim. dec. ca. 170 °C. − IR: $\tilde{\nu}$ = 1595m, 1580m, 1410s, 1308m, 1281m, 1258s, 1172w, 1157w, 1085w, 1070m, 1025w, 1004w, 972w, 957w, 884s, 859s, 804w, 769m, 733m, 704s, 635s cm^{-1}. − ^1H NMR (C_6D_6): δ = 0.57 [s, 4 H, β-H(THF)], 2.12 [s, 4 H, α-H(THF)], 6.84−7.04 (m, 21 H, H4, H3′, H4′, H5′), 7.23 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 6 H, H3, H5), 7.34 (dd, $^3J_{H\text{-}H}$ = 7.5 Hz, $^4J_{H\text{-}H}$ = 1.4 Hz, 12 H, H2′, H6′). − $C_{58}H_{47}O_4Sc$, (852.92): calcd. C 81.67, H 5.55, Sc 5.27; found C 81.57, H 5.84, Sc 5.29.

Attempted Preparation of Tris(2,3,5,6-tetraphenylphenolato)(1,2-dimethoxyethane)ytterbium(III): A mixture of 2,3,5,6-tetraphenylphenol, (2.17 g, 5.45 mmol), bis(pentafluorophenyl)mercury(II) (1.46 g, 2.73 mmol) and ytterbium powder (0.63 g, 3.64 mmol) was stirred in DME (50 mL) at room temperature for 5 h. The reaction mixture turned brown-orange and was stirred for a further 24 h at 70 °C. Filtration gave a dark brown solution which was reduced in volume. Yellow needle-like crystals formed overnight and were dried under vacuum at room temperature (0.65 g, 23% for $[Yb(OAr^{Ph})_3(DME)]\cdot DME$). − IR: $\tilde{\nu}$ = 1597m, 1578w, 1531m, 1346s, 1306s, 1275m, 1143s, 1110m, 1072m, 1043m, 1025m, 952s, 917w, 869w, 840w, 794w, 758s, 699s, 672s cm^{-1}. − Vis/near IR (THF): λ_{max} (ε) = 410 (197), 912 (2), 980 (38) nm ($dm^3\ mol^{-1}\ cm^{-1}$). − $C_{94}H_{73}O_5Yb$ $[Yb(OAr^{Ph})_3(DME)]$ (1299.56): calcd. C 77.56, H 5.06, Yb 11.89; − $C_{98}H_{83}O_7Yb$ $[Yb(OAr^{Ph})_3(DME)_2]$ (1545.68): calcd. C 76.14, H 5.41, Yb 11.19; found C 72.51, H 5.43, Yb 11.20.

Structure Determinations: Full spheres of CCD area-detector data were measured at the specified temperature (Bruker AXS instrument; $2\theta_{max}$ as specified; monochromatic Mo-K_α radiation, λ = 0.7107_3 Å) yielding $N_{t(otal)}$ reflections, reducing to N unique (R_{int} quoted) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed" and used in the full-matrix least-squares refinement (anisotropic thermal parameter forms for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ constrained at estimated values). Conventional residuals R, R_w (weights: $[\sigma^2(F) + 0.0004\ F^2)^{-1}]$ are quoted on $|F|$ at convergence. Neutral atom complex scattering factors were employed within the context of the Xtal 3.4 program system.[22] Pertinent results are given in the figures and tables. In the figures 20% displacement amplitudes are shown for the structures determined at low temperature, 50% for room temperature. Hydrogen atoms have arbitrary radii of 0.1 Å. Individual variations in procedure, idiosyncrasies, difficulties are noted below.

Crystal/Refinement Data

[Yb(OAr^{tBu})$_3$(THF)]·THF: $C_{86}H_{103}O_5Yb$, M = 1389.8. Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 14.930(1), b = 16.601(1), c = 17.281(1) Å, α = 110.491(1)°, β = 99.703(1)°, γ = 104.169(1)°, V = 3735 Å^3. D_c (Z = 2) = 1.23$_6$ g cm^{-3}. μ_{Mo} = 13.0 cm^{-1}; specimen: 0.55 × 0.40 × 0.15 mm; $'T'_{min.,max}$ = 0.61, 0.83. $2\theta_{max}$ = 58°; N_t = 43419, N = 18211 (R_{int} = 0.029), N_o = 12973; R = 0.038, R_w = 0.039. $|\Delta\rho_{max}|$ = 1.37(9) e Å^{-3}. T ca. 300 K. Displacement parameters of the lattice solvent were very large; site occupancy was set at unity after trial refinement.

[Sc(OAr^{tBu})$_3$(THF)]·THF: $C_{86}H_{103}O_5Sc$, M = 1261.7. Triclinic, space group $P\bar{1}$, a = 14.805(2), b = 16.208(2), c = 17.042(2) Å, α = 109.649(2)°, β = 99.719(2)°, γ = 103.981(2)°, V = 3595 Å^3. D_c (Z = 2) = 1.16$_6$ g cm^{-3}. μ_{Mo} = 1.5 cm^{-1}; specimen: 0.25 × 0.20 × 0.04 mm; $'T'_{min.,max}$ = 0.67, 0.82. $2\theta_{max}$ = 58°; N_t = 39461, N = 18825 (R_{int} = 0.079), N_o = 7579; R = 0.062, R_w = 0.055. $|\Delta\rho_{max}|$ = 0.67(6) e Å^{-3}. T ca. 153 K. All hydrogen atoms except those associated with the uncoordinated THF were refined in (x, y, z, U_{iso}).

[Yb(OAr^{Me})$_3$THF]: $C_{64}H_{59}O_4Yb$, M = 1065.2. Triclinic, space group $P\bar{1}$, a = 11.154(1), b = 11.818(1), c = 20.371(2) Å, α = 76.824(2)°, β = 77.809(2)°, γ = 78.415(2)°, V = 2522 Å^3. D_c (Z = 2) = 1.40$_2$ g cm^{-3}. μ_{Mo} = 19.0 cm^{-1}; specimen: 0.35 × 0.17 × 0.10 mm; $'T'_{min.,max}$ = 0.66, 0.83. $2\theta_{max}$ = 58°; N_t = 29447, N = 12359 (R_{int} = 0.028), N_o = 11025; R = 0.046, R_w = 0.065. $|\Delta\rho_{max}|$ = 2.4(1) e Å^{-3}. T ca. 153 K.

[Yb(OAr^{Ph})$_3$DME]·1.5THF: $C_{100}H_{85}O_{6.5}Yb$, M = 1563.8. Monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 13.0079(9), b = 32.407(2), c = 24.860(2) Å, β = 91.798(1)°, V = 10474 Å^3. D_c (Z = 4) = 0.99$_2$ g cm^{-3}. μ_{Mo} = 9.4 cm^{-1}; specimen: 0.30 × 0.25 × 0.10 mm; $'T'_{min.,max}$ = 0.62, 0.86. $2\theta_{max}$ = 58°; N_t = 114947, N = 18408 (R_{int} = 0.098), N_o = 11241; R = 0.060, R_w = 0.090. $|\Delta\rho_{max}|$ = 1.54(6) e Å^{-3}. T ca. 300 K. Lattice solvent residues were modelled as 0.5THF at each of three sites, with constrained geometries and isotropic thermal parameter forms.

[Yb(OAr^{Me})$_2$(THF)$_3$]: $C_{52}H_{58}O_5Yb$, M = 936.1. Monoclinic, space group Cc (C_s^4, no. 9), a = 19.945(1), b = 11.8084(5), c = 19.193(1) Å, β = 97.416(3)°, V = 4482 Å^3. D_c (Z = 4) = 1.38$_7$ g cm^{-3}. μ_{Mo} = 21.2 cm^{-1}; specimen: 0.17 × 0.15 × 0.08 mm; $'T'_{min.,max}$ = 0.50, 0.85. $2\theta_{max}$ = 53°; N_t = 23259, N = 7519 (R_{int} = 0.11; 'Friedel pairs' retained distinct), N_o = 6338; R = 0.053, R_w = 0.093. $|\Delta\rho_{max}|$ = 0.9 e Å^{-3}. T *ca* 193 K. Data were measured using a Nonius Kappa CCD instrument. Refinement was carried out using the SHELX-97 system.[23] The phenyl ring pendant at C(26) was modelled as disordered over two sets of sites of equal occupancy, with isotropic thermal parameter refinement for the carbon atoms. The absolute structure was indeterminate.

[Sc(OAr^H)$_3$]: $C_{54}H_{39}O_3Sc$, M = 780.9. Monoclinic, space group $P2_1/c$, a = 11.261(8), b = 20.10(1), c = 17.81(1) Å, β = 100.02(1)°, V = 3970 Å^3. D_c = 1.30$_6$ g cm^{-3}. μ_{Mo} = 2.3 cm^{-1}; specimen: 0.25 × 0.15 × 0.03 mm; $'T'_{min.,max}$ = 0.59, 0.88. $2\theta_{max}$ = 50°; N_t = 19251, N = 6895 (R_{int} = 0.21), N_o = 1394; R = 0.088, R_w = 0.097. $|\Delta\rho_{max}|$ = 0.86(6) e Å^{-3}. T ca. 153 K. Weak and limited data from a very fragile leaf-like specimen would support meaningful anisotropic thermal parameter form refinement for Sc only, isotropic forms for C, O.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The supplementary publication nos. CCDC-153631, -153627, -153628, -153629, -153626, -153630 apply sequentially to the compounds in the Crystal/Refinement Data section. Copies of the data can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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