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Alkali Metal Induced Structural Changes in Complexes Containing Anionic Lanthanum Aryloxide Moieties. X-ray Crystal Structures of (THF)La(OAr)$_2$(μ-OAr)$_2$Li(THF), (THF)La(OAr)$_2$(μ-OAr)$_2$Na(THF)$_2$, and CsLa(OAr)$_4$ (Ar = 2,6-i-Pr$_2$C$_6$H$_3$)

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Reaction of La$_2$(OAr)$_6$ (**1**, Ar = 2,6-i-Pr$_2$C$_6$H$_3$) with 2 equiv of LiOAr in THF produces the lanthanum tetrakis(aryloxide) salt (THF)La(OAr)$_2$(μ-OAr)$_2$Li(THF) (**2**). A similar reaction employing NaOAr leads to isolation of the analogous sodium salt (THF)La(OAr)$_2$(μ-OAr)$_2$Na(THF)$_2$ (**3**). **1** reacts with 2 equiv of cesium aryloxide in THF to yield the base-free cesium salt CsLa(OAr)$_4$ (**4**). Compounds **2**, **3**, and **4** have been characterized by ^{1}H NMR and IR spectroscopy, microanalysis, and single-crystal X-ray diffraction studies. The overall molecular geometry of **2** comprises a five-coordinate La metal center coordinated by four aryloxide ligands and one THF ligand in a somewhat distorted trigonal bipyramidal geometry and a three-coordinate Li cation which is coordinated to the oxygen atoms of two aryloxide ligands as well as a single THF ligand. La−O bond lengths average 2.208(3) and 2.384(3) Å for terminal and bridging aryloxide ligands, respectively, while the average Li-O(aryloxide) bond distance is 1.866(10) Å. The molecular geometry of **3** is similar to that observed in **2**, with a five-coordinate La metal center displaying a distorted trigonal bipyramidal geometry in which a THF ligand and an aryloxide ligand occupy axial positions. Two of the aryloxide ligands on the La metal center bridge to a sodium cation, which completes its coordination sphere by coordination of two additional molecules of THF. La−O bond lengths average 2.227(6) and 2.333(5) Å for terminal and bridging aryloxide ligands, respectively, while the average Na−OAr bond distance is 2.350(6) Å. The *ipso* carbon atom of one of the bridging aryloxide ligands is directed toward the fifth coordination site of the sodium cation at a distance of 3.085(9) Å. The solid state structure of CsLa(OAr)$_4$ (**4**) features alternating tetrahedral [La(OAr)$_4$]$^-$ anions (La−O = 2.241(6) Å (ave.)) and Cs$^+$ cations held in an extended structure by means of cesium−π-arene interactions, resulting in the formation of a quasi one-dimensional infinite chain structure. The cesium environment in **4** consists exclusively of multihapto Cs−C interactions (Cs−C range 3.696(7)−3.847(7) Å), with no Cs−O contacts of less than 4.649 Å. Crystal data for **2** (at −100 °C): orthorhombic space group *Pbca*, $a = 20.091(3)$ Å, $b = 19.983(2)$ Å, $c = 27.288(2)$ Å, $V = 10956$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.202$ g cm^{-3}. Crystal data for **3** (at −100 °C): orthorhombic space group *Pbca*, $a = 26.035(3)$ Å, $b = 20.771(4)$ Å, $c = 26.441(3)$ Å, $V = 14299$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.174$ g cm^{-3}. Crystal data for **4** (at −100 °C): monoclinic space group *C*2/*c*, $a = 21.261(2)$ Å, $b = 22.616(3)$ Å, $c = 20.740(2)$ Å, $\beta = 108.126(7)°$, $V = 9478$ Å^3, $Z = 8$, $D_{\text{calc}} = 1.465$ g cm^{-3}.

Introduction

The preparation of inorganic and organometallic complexes of the lanthanide elements *via* the addition of an alkali metal reagent to a lanthanide halide derivative is a cornerstone of synthetic methodology in this field.[2] In many cases, the reactions proceed in a straightforward manner to produce the desired target molecule in high yield with no undesirable side reactions. However, there are a large number of documented cases, particularly when utilizing reagents containing the smaller alkali metals (M = Li, Na), in which the isolated reaction products contain one, two, or more equivalents of an alkali metal salt bound within the coordination sphere of the lanthanide metal, resulting in the formation of salt or "ate" complexes. This phenomenon has been widely observed during syntheses of alkyl,[3] alkoxide,[4] amide,[5] thiolate,[6] cyclopentadienyl,[7] and related complexes[8] of the lanthanide elements.

We have reported previously that the formation of "ate" or "double alkoxide" salts of the f-elements may be somewhat mitigated by the use of potassium reagents,[9b,c,e] purportedly due to the greater insolubility of KCl in typical organic solvents

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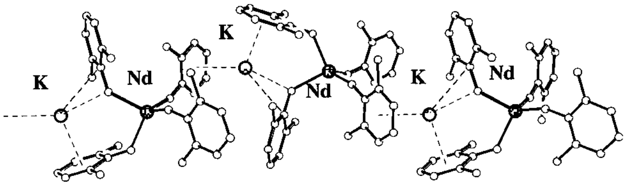
compared to that of LiCl and NaCl. However, even the use of heavier alkali metal reagents has not completely eliminated the problem of salt retention. Thus the room temperature reaction of anhydrous $LnCl_3$ (Ln = Nd, Er, Lu) with 3 or 4 equiv of potassium 2,6-diisopropylphenoxide in THF leads to the formation of potassium salts of formula $KLn(OAr)_4$, according to the stoichiometry of eq 1.[9a,f]

$$LnCl_3 + 4KOAr \xrightarrow{THF} KLn(OAr)_4 + 3KCl \qquad (1)$$

$$Ln = Nd, Er, Lu; \quad Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$$

These salts exhibit unusual solid state structures involving multihapto π-arene interactions between the aryloxide ligands and potassium cations. The presence of K−C interactions between adjacent $[Ln(OAr)_4]^-$ units leads to the formation of pseudo-one-dimensional infinite chains, as shown in **I** for the neodymium salt $KNd(OAr)_4$. A similar structural motif has also been observed in the recently-reported lanthanide aryloxide complexes $\{K[(\mu\text{-}\eta\text{-}C_5H_5)_2Nd(\mu\text{-}O\text{-}2,6\text{-}Me_2C_6H_3)_2]\}_n$[10a] and $\{K[Sm(\mu\text{-}O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_3(THF)]\}_n$,[10b] and related alkali metal−π-arene interactions have been documented in a number of recent publications.[11]



I

Detailed computational studies have recently been performed concerning the interaction of alkali metal cations with both neutral arene rings[12a,b] and delocalized carbanions.[11i,12c] These calculations have shown that the larger, more polarizable cations, potassium through cesium, prefer multihapto interactions with ring carbons while the smaller alkali metals, particularly lithium, tend to interact with the center of highest charge.[11i,12c] Collateral interactions with additional carbanions were also found to be energetically favorable for the heavier alkali metals, in contrast to lithium and sodium cations which favored interactions with heteroatoms such as nitrogen and oxygen.

On the basis of expected differences in coordination environment upon moving from lithium to cesium and having noted recent publications which describe the significant structural and reactivity effects of varying the alkali metal cation in a series of anionic cobalt and chromium aryloxide derivatives,[13,14] we undertook an investigation of a series of lanthanum salt complexes of general formula $M[Ln(OAr)_4]$ (M = Li, Na, Cs; Ar = 2,6-i-$Pr_2C_6H_3$). Together with the known structure of the potassium analog, the results allow a general picture of the effects of different alkali metal cations upon the extended solid state structures of anionic lanthanide aryloxide complexes to be developed.

Results and Discussion

Synthesis and Reactivity. Initial investigations were directed toward optimization of a suitable synthetic strategy for the preparation of the desired lanthanum salt complexes of general formula $MLa(OAr)_4$ (M = Li, Na, Cs; Ar = 2,6-i-$Pr_2C_6H_3$). It was found that the reaction of anhydrous $LaCl_3$ with 4 equiv of alkali metal aryloxide in THF produced mixtures of products which proved difficult to separate. It is postulated that these mixtures contain both neutral and anionic chloride/aryloxide species of the type $LaCl_x(OAr)_{3-x}$ and $KLaCl_x(OAr)_{4-x}$. Subsequently, we focused on the reaction of a preformed tris(aryloxide) species with an additional 1 equiv of alkali metal aryloxide. We have previously reported the synthesis of the homoleptic lanthanide aryloxide complexes $Ln_2(OAr)_6$ (Ln = La, Nd, Sm, Er) *via* the synthetic route shown in eq 2.[9d,g]

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$$2\mathrm{Ln}[\mathrm{N}(\mathrm{SiMe}_3)_2]_3 + 6\mathrm{HOAr} \xrightarrow{\text{toluene}} \mathrm{Ln}_2(\mathrm{OAr})_6 + 6\mathrm{HN}(\mathrm{SiMe}_3)_2 \quad (2)$$

$$\mathrm{Ar} = 2,6\text{-}i\text{-}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$$

It was found that the reaction of THF soluble $La_2(OAr)_6$ with 2 equiv of MOAr (M = Li, Na, Cs) consistently provided a more reliable and higher-yielding synthetic route to lanthanide "ate" complexes than did the reaction of the rather insoluble $LaCl_3$ with 4 equiv of the aryloxide salt. Thus the reaction of $La_2(OAr)_6$ (**1**) with 2 equiv of lithium 2,6-diisopropylphenoxide in THF solution at room temperature for 72 h, followed by crystallization from hexane, produced the lithium "ate" complex $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ (**2**) in 49% yield as shown in eq 3. Compound **2** was found to be slightly soluble in hexane and highly soluble in toluene and benzene. A directly analogous reaction in which **1** was allowed to react with 2 equiv of sodium aryloxide resulted in the isolation, following crystallization from toluene, of the sodium "ate" complex $(THF)La(OAr)_2(\mu\text{-}OAr)_2Na(THF)_2$ (**3**) (eq 3). The sodium salt **3** was found to be moderately soluble in toluene and benzene.

$$\underset{(\mathbf{1})}{\mathrm{La}_2(\mathrm{OAr})_6} + 2\mathrm{MOAr} \xrightarrow{\text{THF}} 2(\mathrm{THF})\mathrm{La}(\mathrm{OAr})_2(\mu\text{-}\mathrm{OAr})_2\mathrm{M}(\mathrm{THF})_x \quad \begin{matrix} \mathrm{M} = \mathrm{Li}\ (\mathbf{2}),\ x = 1 \\ \mathrm{M} = \mathrm{Na}\ (\mathbf{3}),\ x = 2 \end{matrix} \quad (3)$$

$$\mathrm{Ar} = 2,6\text{-}i\text{-}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$$

The reaction of $La_2(OAr)_6$ with 2 equiv of cesium 2,6-diisopropylphenoxide in THF solution at room temperature for 72 h, followed by dissolution into hot toluene and crystallization, yielded the THF-free cesium salt complex $CsLa(OAr)_4$ (**4**) (eq 4). Compound **4** was found to be slightly soluble in toluene and moderately soluble in THF. ^1H NMR spectroscopy confirmed the absence of THF ligands in this complex, and microanalytical data are consistent with the proposed stoichiometry of $CsLa(OAr)_4$.

$$\underset{(\mathbf{1})}{\mathrm{La}_2(\mathrm{OAr})_6} + 2\mathrm{CsOAr} \xrightarrow{\text{THF}} \underset{(\mathbf{4})}{2\mathrm{CsLa}(\mathrm{OAr})_4} \quad (4)$$

$$\mathrm{Ar} = 2,6\text{-}i\text{-}\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$$

Solid State and Molecular Structures. Three heterometallic 2,6-diisopropylphenoxide complexes have been examined by single-crystal X-ray diffraction techniques during the course of this work: $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ (**2**), $(THF)La(OAr)_2(\mu\text{-}OAr)_2Na(THF)_2\cdot(C_7H_8)_2$ (**3**), and $CsLa(OAr)_4$ (**4**). A summary of data collection and crystallographic parameters is given in Table 1.

Table 1. Summary of Crystal Data[a]

	2	**3**	**4**
empirical formula	$LiLaC_{56}H_{85}O_6$	$NaLaC_{74}H_{100}O_7$	$CsLaC_{48}H_{68}O_4$
space group	*Pbca*	*Pbca*	*C*2/*c*
a, Å	20.091(3)	26.035(3)	21.261(2)
b, Å	19.983(2)	20.771(4)	22.616(3)
c, Å	27.288(2)	26.441(3)	20.740(2)
β, deg			108.126(7)
T, °C	−100	−100	−100
Z (mol/unit cell)	8	8	8
V, Å^3	10956	14299	9478
D_{calcd}, g cm^{-3}	1.202	1.174	1.465
λ (Mo Kα)	0.71069	0.71069	0.71069
fw	991.02	1263.44	1044.84
abs coeff, cm^{-1}	8.24	6.52	17.1
R(*F*)[b]	0.0457	0.0659	0.0385
$R2_w$	0.1049	0.1207	0.0757

[a] **2** = $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$; **3** = $(THF)La(OAr)_2(\mu\text{-}OAr)_2Na(THF)_2\cdot(C_7H_8)_2$; **4** = $CsLa(OAr)_4$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ (**2**)

La(1)−O(1)	2.213(3)	La(1)−O(5)	2.608(3)
La(1)−O(2)	2.376(3)	Li(1)−O(2)	1.857(10)
La(1)−O(3)	2.204(3)	Li(1)−O(4)	1.875(9)
La(1)−O(4)	2.392(3)	Li(1)−O(6)	1.871(9)
Li(1)−O(2)−La(1)	95.7(3)	Li(1)−O(4)−La(1)	94.7(3)
O(1)−La(1)−O(2)	103.20(12)	O(1)−La(1)−O(3)	112.34(13)
O(1)−La(1)−O(4)	121.88(12)	O(1)−La(1)−O(5)	81.31(12)
O(2)−La(1)−O(3)	103.80(13)	O(2)−La(1)−O(4)	71.99(11)
O(2)−La(1)−O(5)	154.50(12)	O(3)−La(1)−O(4)	125.24(13)
O(3)−La(1)−O(5)	97.33(13)	O(4)−La(1)−O(5)	84.24(11)
C(1)−O(1)−La(1)	172.2(3)	C(9)−O(2)−La(1)	130.1(3)
C(17)−O(3)−La(1)	170.8(3)	C(25)−O(4)−La(1)	143.2(3)
O(2)−Li(1)−O(4)	97.3(4)	O(2)−Li(1)−O(6)	131.3(5)
O(4)−Li(1)−O(6)	131.4(5)	C(9)−O(2)−Li(1)	131.9(4)
C(25)−O(4)−Li(1)	122.0(4)		

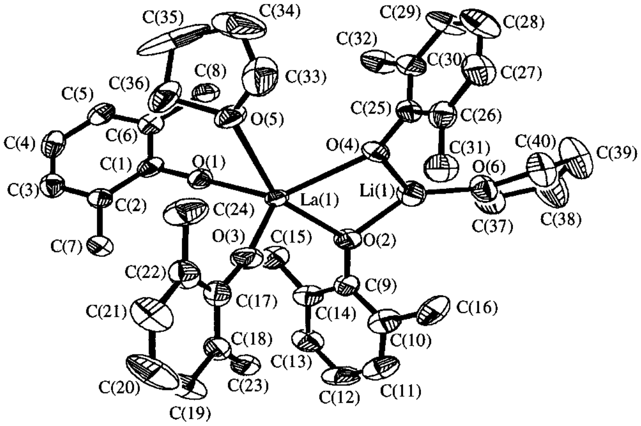

Figure 1. ORTEP plot (50% probability ellipsoids) showing the molecular structure of $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ (**2**) and giving the atom-numbering scheme used in the tables. Methyl carbon atoms of the *iso*-propyl groups are omitted for clarity.

$(THF)La(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2(\mu\text{-}O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2Li(THF)$ (2). Crystals of **2** suitable for an X-ray diffraction study were grown by cooling a concentrated hexane solution to −40 °C. Selected bond lengths and angles are presented in Table 2. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 1. The overall molecular geometry comprises a five-coordinate lanthanum metal center, which is coordinated by four aryloxide ligands and one THF ligand in a somewhat distorted trigonal bipyramidal geometry and a three-coordinate lithium cation which is coordinated to the oxygen atoms of two aryloxide ligands as well as a single THF ligand (Figure 1). The overall molecular structure of **2** is thus similar to that of the previously-reported vanadium(III) salt complex $V(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ ($Ar = 2,6\text{-}i\text{-}Pr_2C_6H_3$).[15a] The THF ligand and the aryloxide ligand containing O(2) are considered to occupy axial positions within the trigonal bipyramidal geometry about the La metal center, and the O(2)−La(1)−O(5) angle is distorted away from the idealized 180° to 154.50(12)°, presumably due to steric demands of the bridging aryloxide ligand. The O−La−O angles within the equatorial plane sum to 359.5°, indicating near planarity of the equatorial ligand set.

Terminal La−O bond lengths average 2.208(3) Å, which falls within the range previously reported for terminal La−O

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (THF)La(OAr)$_2$(μ-OAr)$_2$Na(THF)$_2$·(C$_7$H$_8$)$_2$ (**3**)

La(1)−O(1)	2.323(5)	La(1)−O(2)	2.224(6)
La(1)−O(3)	2.229(6)	La(1)−O(4)	2.343(5)
La(1)−O(5)	2.625(5)	Na(1)−O(1)	2.362(6)
Na(1)−O(4)	2.339(6)	Na(1)−O(7)	2.291(7)
Na(1)−O(8)	2.280(7)	Na(1)−C(13)	3.085(9)

La(1)−O(1)−Na(1)	99.4(2)	La(1)−O(4)−Na(1)	99.5(2)
O(1)−La(1)−O(2)	106.1(2)	O(1)−La(1)−O(3)	103.4(2)
O(1)−La(1)−O(4)	79.6(2)	O(1)−La(1)−O(5)	160.6(2)
O(2)−La(1)−O(3)	112.5(2)	O(2)−La(1)−O(4)	124.9(2)
O(2)−La(1)−O(5)	89.0(2)	O(3)−La(1)−O(4)	119.3(2)
O(3)−La(1)−O(5)	81.3(2)	O(4)−La(1)−O(5)	81.7(2)
C(13)−O(1)−La(1)	151.8(5)	C(7)−O(2)−La(1)	171.1(6)
C(1)−O(3)−La(1)	171.6(6)	C(19)−O(4)−La(1)	141.3(5)
O(1)−Na(1)−O(4)	78.9(2)	O(1)−Na(1)−O(7)	151.0(3)
O(1)−Na(1)−O(8)	103.0(3)	O(4)−Na(1)−O(7)	104.8(3)
O(4)−Na(1)−O(8)	145.4(3)	O(7)−Na(1)−O(8)	90.1(3)
O(1)−Na(1)−C(13)	24.8(2)	O(4)−Na(1)−C(13)	103.2(2)
O(7)−Na(1)−C(13)	136.1(3)	O(8)−Na(1)−C(13)	85.6(3)
C(13)−O(1)−Na(1)	108.8(5)	C(19)−O(4)−Na(1)	115.7(5)

distances of 2.193(5)−2.290(9) Å.[4a,9g,16,17] La−O distances to the bridging ligands are, as expected, somewhat longer at 2.384(3) Å (ave.). The O−La−O bond angle between the two terminal aryloxide ligands is fairly close to the 120° value expected for two ligands within the equatorial plane (O(1)−La(1)−O(3) = 112.34(13)°), whereas the O(2)−La(1)−O(4) angle between the two aryloxide ligands which bridge to the lithium cation is dramatically smaller at 71.99(11)°. The La−O−C bond angles for the bridging aryloxide ligands are rather acute at 130.1(3) and 143.2(3)°, reflecting their interaction with the lithium cation, while the La−O−C bond angles for the terminal aryloxide ligands are typically more obtuse and average 171.5(3)°.

The coordination geometry of the lithium cation is trigonal planar, a geometry which has been reported for a number of other lithium salt complexes. The average Li−O(aryloxide) bond distance of 1.866(10) Å lies at the lower end of the range previously reported for Li−OAr bonds of 1.811(17)−1.995(12) Å and most likely reflects the low coordination number of the lithium metal center.[18] The O−Li−O bond angle between the bridging aryloxide ligands is 97.3(4)°, while the two O−Li−O angles between the THF and the bridging aryloxide ligands average 131.3(5)°. The three O−Li−O angles sum to 360°, indicating almost perfect planarity of the lithium cation and the three coordinated oxygen atoms. The nonbonding La−Li distance within the dimer is 3.158(9) Å.

(THF)La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(μ-O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$Na(THF)$_2$·(C$_7$H$_8$)$_2$ (3). Single crystals of **3** were grown from a concentrated toluene solution at −40 °C. Selected bond lengths and angles are presented in Table 3. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 2. Compound **3** crystallizes in the orthorhombic space group *Pbca*, and no unusual intermolecular contacts are seen in the solid state. The overall molecular geometry is similar to that observed in the lithium complex **2**, with a five-coordinate lanthanum metal center displaying a distorted trigonal bipyramidal geometry in which a THF ligand and an aryloxide ligand occupy axial positions. Two of the aryloxide ligands on the lanthanum metal center bridge to a sodium cation, which completes its coordination sphere by coordination of two additional molecules of THF (Figure 2). The axial O(5)−La−O(1) angle is distorted from 180 to 160.6(2)°, while the O−La−O angles in the equatorial plane sum to 356.7°. The La−O bond lengths average 2.227(6) Å for terminal ligands and 2.333(5) Å for bridging aryloxide ligands and are within the range of La−O distances reported above. As previously observed in the structure of **2** (*vide supra*), the O−La−O angle between the bridging aryloxide ligands [O(1)−La−O(4) = 79.6(2)°] is much smaller than that between the two terminal aryloxide ligands [O(2)−La−O(3) = 112.5(2)°]. The La−O−C bond angles for the bridging aryloxide ligands are 141.3(5) and 151.8(5)°, while the La−O−C angles for the terminal aryloxide ligands average 171.4(6)°.

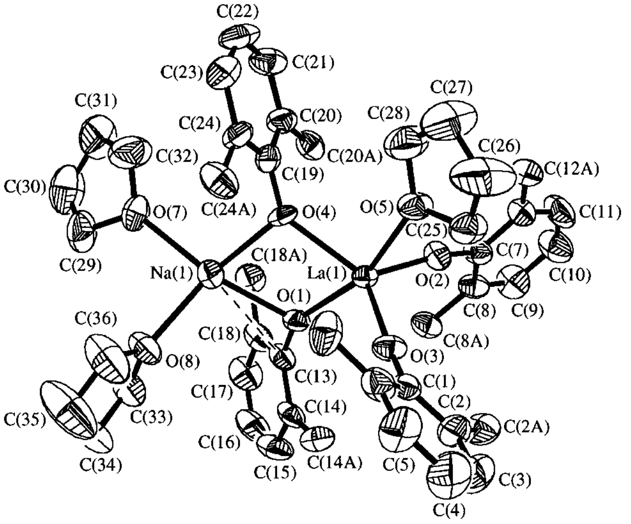

Figure 2. ORTEP plot (50% probability ellipsoids) showing the molecular structure of (THF)La(OAr)$_2$(μ-OAr)$_2$Na(THF)$_2$ (**3**) and giving the atom-numbering scheme used in the tables. Methyl carbon atoms of the *iso*-propyl groups are omitted for clarity.

The sodium cation is bound to the oxygen atoms of two bridging aryloxide ligands in addition to two terminal THF ligands. Furthermore, the *ipso* carbon atom of one of the bridging aryloxide ligands is directed toward the fifth coordination site of the sodium cation at a relatively long bond distance of 3.085(9) Å. This coordination geometry is similar to that documented previously for [Na(TMEDA)]$_2$[Cr(O-2,6-Me$_2$C$_6$H$_3$)$_4$], which also contains a long Na−C interaction with one of the methyl carbons bound to the aromatic ring.[13b] The average Na−OAr bond distance of 2.350(6) Å lies within the range previously reported for Na−OAr distances of 1.811(17)−2.842(5).[11j,m,19] The O−Na−O bond angle between the bridging aryloxide ligands is 78.9(2)° while the O−Na−O angle between the two THF ligands is 90.1(3)°. The nonbonding La−Na distance within the dimer is 3.573(3) Å.

In complexes **2** and **3** it is notable that the lanthanum metal center coordinates a molecule of THF in addition to the four aryloxide ligands to produce a five-coordinate metal center, rather than the pseudotetrahedral lanthanum metal centers observed in **4** (*vide infra*) and KLa(OAr)$_4$.[9f] A possible

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Table 4. Selected Bond Lengths (Å) and Angles (deg) for $CsLa(OAr)_4$ (**4**)[a]

La(1)−O(1)	2.251(4)	La(1)−O(2)	2.231(5)
La(2)−O(3)	2.240(5)	La(2)−O(4)	2.248(4)
Cs(1)−C(8)	3.809(7)	Cs(1)−C(9)	3.696(7)
Cs(1)−C(10)	3.748(7)	Cs(1)−C(16)	3.716(7)
Cs(1)−C(17)	3.684(7)	Cs(1)−C(18)	3.847(7)
Cs(2)−C(2)	3.807(6)	Cs(2)−C(3)	3.651(7)
Cs(2)−C(4)	3.710(7)	Cs(2)−C(26)	3.771(7)
Cs(2)−C(27)#1	3.622(7)	Cs(2)−C(28)#1	3.700(7)
O(1)−La(1)−O(1)#1	110.8(2)	O(1)−La(1)−O(2)	108.7(2)
O(1)−La(1)−O(2)#1	111.4(2)	O(2)−La(1)−O(2)#1	105.9(3)
O(3)−La(2)−O(3)#1	106.5(2)	O(3)−La(2)−O(4)	110.5(2)
O(3)−La(2)−O(4)#1	110.1(2)	O(4)−La(2)−O(4)#1	109.0(2)
C(1)−O(1)−La(1)	149.6(4)	C(7)−O(2)−La(1)	156.1(5)
C(25)#2−O(3)−La(2)	154.1(4)	C(13)−O(4)−La(2)	150.9(4)

[a] Symmetry transformation used to generate equivalent atoms: #1 $-x, y, -z + 1/2$, #2 $x, y + 1, z$.

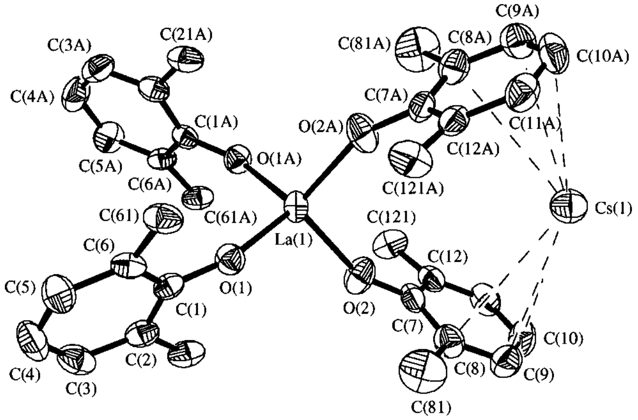

Figure 3. ORTEP plot (50% probability ellipsoids) showing the solid state structure of $CsLa(OAr)_4$ (**4**), emphasizing the multihapto interaction between the cesium cation and the arene rings of the aryloxide ligands. Methyl carbon atoms of the *iso*-propyl groups are omitted for clarity.

explanation for this results from a consideration of the oxygen-bridging configurations of complexes **2** and **3**. The O−La−O bond angles for the bridging aryloxides of $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ (**2**) and $(THF)La(OAr)_2(\mu\text{-}OAr)_2Na(THF)_2$ (**3**) are greatly reduced from a typical tetrahedral value down to 71.99(11) and 79.6(2)°, respectively. This significant deformation of bond angle effectively makes available an additional coordination site which is filled by the THF ligand.

$CsLa(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_4$ (4). Crystals of **4** suitable for an X-ray diffraction study were grown from a concentrated toluene solution upon slow evaporation under a helium atmosphere. Selected bond lengths and angles are presented in Table 4. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 3. The solid state structure of $CsLa(OAr)_4$ (**4**) shows an overall similarity to that of the previously-reported potassium analog $KLa(OAr)_4$,[9f] in that it features alternating $[La(OAr)_4]^-$ anions and Cs^+ cations held in an extended structure by means of cesium−π-arene interactions. However, these interactions result in the formation of a quasi one-dimensional infinite chain bridged by cesium−η-arene interactions (Figure 4), rather than the pseudo-two-dimensional sheet structure observed in $KLa(OAr)_4$.[9f] This one-dimensional chain configuration is very similar to that observed in the structures of $KLn(OAr)_4$ (Ln = Nd, Er), which possess one-dimensional infinite chain structures differing only in the number of alkali metal interactions which bridge the subunits.[9f] The $KLn(OAr)_4$ (Ln = Nd, Er) complexes also feature potassium interactions with oxygen atoms of the aryloxide ligands while **4** does not feature any meaningful Cs−O contacts (*vide infra*).

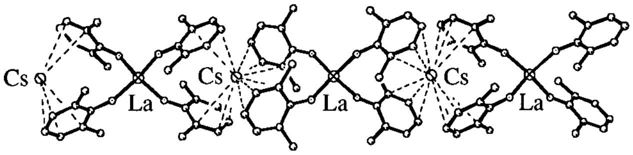

Figure 4. Ball-and-stick drawing of the extended quasi one-dimensional infinite chain structure of $CsLa(OAr)_4$ (**4**). Methyl carbon atoms of the *iso*-propyl groups are omitted for clarity.

The lanthanum metal center in **4** displays a pseudotetrahedral coordination environment with O−La−O angles very close to ideal, ranging from 105.9(3) to 111.4(2)°. The average La−O distance of 2.241(6) Å is directly comparable to the distances found in **2** and **3**. The cesium environment in the solid state structure of **4** consists *exclusively* of multihapto Cs−C interactions, with no Cs−O contacts of less than 4.649 Å being present within the structure (Figure 4). This coordination environment bears comparison with that found in [Cs(4-*tert*-butylcalix-4-arene)(MeCN)],[20a] in which the cesium cation interacts with arene moieties (Cs−C = 3.545(3)−4.121(4) Å) but makes no Cs−O contacts shorter than 4.0 Å. The cesium cation in **4** exhibits four principal η^3-arene interactions with the phenyl rings containing C(16)−C(18) and C(16a)−C(18a) (Cs−C range 3.716(7)−3.847(7) Å) and C(8)−C(11) and C(8a)−C(11a) (Cs−C range 3.696(7)−3.809(7) Å). These Cs−C distances lie within the range of 3.35(4)−4.12(1) Å found in other structurally characterized complexes containing Cs−arene interactions.[11i,k,20] The shortest nonbonding Cs−La distance within the structure is 5.637 Å.

Spectroscopic Characterization. ^{1}H NMR spectroscopy. $(THF)La(OAr)_2(\mu\text{-}OAr)_2Li(THF)$ (2). Ambient temperature ^{1}H NMR spectra of **2** in benzene-d_6 solution reveal only one aryloxide and one THF ligand environment, in a 2:1 ratio. At room temperature the α-THF protons are observed as a broad resonance at δ 3.14. However, when a toluene-d_8 solution of **2** was cooled to −80 °C, this resonance decoalesces into two broad resonances at δ 3.57 and 2.54. Overlap of the resonance at 3.57 ppm with a resonance at 3.44 ppm, which is assigned to the isopropyl methine protons, precluded accurate integration of the two THF resonances. The resonance at δ 3.57 is assigned to the α-protons on the THF bound to the lanthanum metal center, and the chemical shift agrees well with the values for several other lanthanum−THF adducts.[4a,11e,21] The resonance at δ 2.54 is assigned to the α-protons on the THF bound to the lithium cation, and integration reveals a ratio of one lithium-

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bound THF to four aryloxide ligands. The β-THF resonances display similar, although less marked, temperature-dependent behavior. At room temperature the β-THF protons appear as a broad resonance at 0.95 ppm, whereas at −80 °C this resonance decoalesces into two separate resonances which show a temperature-dependent shift upfield to 0.681 and 0.58 ppm.

The aromatic proton resonances and the *iso*-propyl methine resonance of the aryloxide ligand broaden upon cooling to −80 °C and show more complex splittings, but do not decoalesce into assignable bridging and terminal resonances. However, at −80 °C the *iso*-propyl methyl resonances show the presence of a broad doublet at 1.33 ppm and a broad singlet at 1.22 ppm. The close proximity of the resonances for the two types of methyl group environments, as well as their equivalent integrations, prevents assignment of terminal and bridging aryloxide ligands, but the 1:1 ratio is consistent with maintenance of the bridging structure in solution.

(THF)La(OAr)$_2$(μ-OAr)$_2$Na(THF)$_2$ (3). Ambient temperature ^{1}H NMR spectra of **3** in benzene-d_6 solution reveal only one type of aryloxide and one type of THF ligand environment, in a 4:3 ratio. At −80 °C, however, it is possible to discern two types of α-THF resonances at 3.50 and 2.52 ppm. Integration of these resonances support the assignment of the downfield resonances to the α-protons on the THF coordinated to the lanthanum and the upfield resonances to the two THF ligands bound to sodium.

In **3**, the β-THF resonances do not separate out into two distinct types; however, they do shift significantly upfield upon cooling. At ambient temperature these protons resonate at 1.21 ppm while at −80 °C they are shifted to 0.86 ppm.

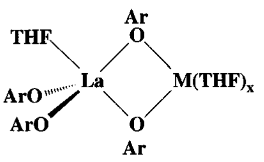
CsLa(OAr)$_4$ (4). The ambient temperature ^{1}H NMR spectrum of **4** in benzene-d_6 reveals only one type of aryloxide ligand environment in solution. The aromatic resonances are shifted upfield from those of complexes **2** and **3.** The shielding effect (and upfield shifting of the aromatic resonances) is found to be greater in the cesium complex **4** than in the potassium analog KLa(OAr)$_4$.[9f] These results are consistent with changes expected due to shielding of the aromatic rings by the large alkali metal cations but do not rule out the possibility of separate ion pairs in solution.

Infrared Spectroscopic Studies. Solid state IR spectra of the heterometallic complexes (THF)La(OAr)$_2$(μ-OAr)$_2$Li(THF) (**2**) and (THF)La(OAr)$_2$(μ-OAr)$_2$Na(THF)$_2$ (**3**) are rather similar in appearance, and both exhibit aromatic C═C stretches at 1588 cm^{-1}. In the case of KLa(OAr)$_4$ and CsLa(OAr)$_4$, however, subtle shifts of the C═C stretch to lower energy (1581 and 1583 cm^{-1}, respectively) are observed. This is suggestive of a slight decrease in aromatic C═C bond strength due to donation of electron density from the aromatic π-cloud to the alkali metal cations.

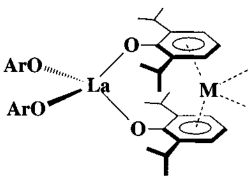
A band consistent with THF coordination is seen at 855 and 852 cm^{-1} in the IR spectra of **2** and **3**, respectively. This band can be compared with those seen in UI$_3$(THF)$_4$, UBr$_3$(THF)$_4$, NpI$_3$(THF)$_4$, and PuI$_3$(THF)$_4$ which show similar bands for coordinated THF in the region from 856 to 847 cm^{-1}.[22]

Concluding Remarks

The initial synthesis of pseudo-one-dimensional chain complexes of the type KLn(OAr)$_4$ (Ln = Nd, Er, Lu)[9a,f] led to the present investigation as to the generality of this type of extended structure as the alkali metal was systematically varied from lithium to cesium. The work described here has clearly demonstrated that the nature of the products isolated from reaction of La$_2$(OAr)$_6$ with alkali metal aryloxide salts is highly dependent upon the alkali metal employed. In the case of the smaller alkali metals, lithium and sodium, discrete “double alkoxide” or “ate” complexes are isolated, in which the aryloxide ligand forms an oxygen donor bridge to the alkali metal atom (**II**). The use of potassium or cesium aryloxide, however, leads to the formation of complexes with extended one- or two-dimensional structures bridged by η-arene interactions (**III**).



II



III

The strong preference of lithium and sodium to interact with oxygen atoms of the aryloxide ligands rather than the aromatic π-electron density would appear to be in agreement with simple electrostatic arguments, which would postulate that the relatively “hard” lithium and sodium cations (high charge/size ratio) would preferentially interact with a site of more concentrated electron density (oxygen lone pairs of aryloxide or THF ligands). Conversely, the softer potassium and cesium cations interact exclusively with arene rings of the aryloxide ligands, despite the fact that the preparative reactions were carried out in a donor solvent (THF). In fact, the alkali metal environments of the complexes synthesized in these experiments show striking similarities with the calculated coordination environments of the alkali metal benzyl complexes (MCH$_2$Ph, M = Li−Cs) reported by Schleyer *et al.*[12c] In that work it was found that the smaller alkali metals favored interactions with the center of greatest charge and the presence of additional hard donor ligands to complete their coordination spheres, whereas the larger, softer alkali metals (potassium−cesium) were found to favor polyhapto interactions with the aromatic ring.

During the course of this work, it has been found that the stoichiometry of the preparative reactions may be controlled much more effectively when a highly-soluble species such as La$_2$(OAr)$_6$ (**1**) is used as starting material rather than anhydrous LaCl$_3$, which is virtually insoluble in THF. This is a phenomenon which has been noted on many previous occasions during the synthesis of f element complexes.[9f,23−25] It seems likely that the limited solubility of LaCl$_3$ in THF leads to a situation in which the small quantity of LaCl$_3$ in solution is actually exposed to a large local excess of alkali metal aryloxide (all of which dissolves readily in THF) and thus the reaction can proceed beyond the formation of MLa(OAr)$_4$ to produce M$_2$La(OAr)$_5$.[26] A similar explanation has been proposed for the unexpected formation of other lanthanide and actinide “double alkoxide” and “ate” complexes.[9f]

The results discussed here are the beginnings of a fundamental knowledge of a newly emerging class of heterometallic lanthanide compounds. The applicability of the calculations of

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Schleyer to anionic lanthanide aryloxide systems and the possible generality of these observations to other heterometallic complexes are of great significance. Further studies of the extended solid state structures of lanthanide aryloxide complexes containing heavier alkali metal cations are currently underway.

Experimental Section

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. 2,6-Diisopropylphenol was purchased from Aldrich and degassed before use. La$_2$(OAr)$_6$ was prepared as previously described.[9g] Cesium 2,6-diisopropylphenoxide was prepared from reaction of cesium metal (Aldrich) with 2,6-diisopropylphenol in THF. NaH was obtained as a 60% dispersion in mineral oil, washed with hexane, filtered, and vacuum dried. Solvents were degassed and distilled from sodium benzophenone ketyl under nitrogen. Benzene-*d*$_6$, THF-*d*$_8$, and toluene-*d*$_8$ were degassed, dried over Na−K alloy, and then trap-to-trap distilled before use.

NMR spectra were recorded at 22 °C on Brüker WM300 or Varian Unity 300 spectrometers. All ^{1}H NMR chemical shifts are reported in ppm relative to the ^{1}H impurity in benzene-*d*$_6$, THF-*d*$_8$, or toluene-*d*$_8$ set at δ 7.15, 3.58, or 2.09, respectively. Infrared spectra were recorded on a Digilab FTS-40 spectrometer. Solid state 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.

(THF)La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(*μ*-O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$Li(THF) (2). In the drybox, a solution of La$_2$(OAr)$_6$ (0.50 g, 0.37 mmol) in toluene (25 mL) was added to a stirred solution of lithium 2,6-diisopropylphenoxide, prepared by addition of 0.44 mL (0.74 mmol) of 1.7 M *tert*-butyllithium to 0.13 g (0.74 mmol) of 2,6-diisopropylphenol in THF. Vigorous stirring was continued for 72 h at room temperature. The resulting clear, pale yellow solution was filtered through Celite, and volatiles were removed *in vacuo* to yield an off-white solid. The solid was extracted with 50 mL of hexane and filtered through Celite. The volume of the filtrate was reduced to 20 mL *in vacuo*, and the flask was then cooled to −40 °C. Clear colorless crystals were deposited overnight. Yield: 0.361 g (49%). ^{1}H NMR (300 MHz, benzene-*d*$_6$, 298 K): δ 7.14 (d, $J = 8$ Hz, 2 H, *meta* OAr), 6.88 (t, $J = 8$ Hz, 1 H, *para* OAr), 3.56 (septet, $J = 7$ Hz, 2 H, C*H*Me$_2$), 3.14 (br m, 2 H, α-THF), 1.29 (d, $J = 7$ Hz, 12 H, CH*Me*$_2$), 0.95 (br m, 2 H, *β*-THF). ^{1}H NMR (300 MHz, toluene-*d*$_8$, 193 K): δ 7.10 (br, 2 H, *meta* OAr), 6.94 (br, 1 H, *para* OAr), 3.57 (br m, 1 H, α-THF−La), 3.44 (br, 2 H, C*H*Me$_2$), 2.54 (br m, 1 H, α-THF−Li), 1.33 (d, $J = 6$ Hz, 6 H, CH*Me*$_2$), 1.22 (br, 6 H, CH*Me*$_2$), 0.68 (br m, 1 H, *β*-THF), 0.58 (br m, 1 H, *β*-THF). IR (cm^{-1}): 1588 (m), 1429 (s), 1378 (m), 1359 (w), 1325 (m), 1278 (sh, w), 1259 (s), 1199 (m), 1157 (w), 1143 (w), 1109 (w), 1097 (w), 1056 (w), 1040 (m), 1033 (m), 1025 (m), 953 (w), 944 (sh, w), 935 (w), 919 (w), 885 (m), 855 (m), 839 (m), 804 (w), 795 (w), 756 (s), 752 (s), 728 (w), 722 (sh, w), 689 (m), 683 (m), 668 (w), 616 (w), 595 (w), 555 (m), 527 (m), 428 (m). Anal. Calcd for C$_{56}$H$_{84}$LiLaO$_6$: C, 67.32; H, 8.47. Found: C, 66.41; H, 8.34.

(THF)La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(*μ*-O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$Na(THF)$_2$ (3). In the drybox, a solution of La$_2$(OAr)$_6$ (0.996 g, 0.74 mmol) in toluene (30 mL) was added to a solution of sodium 2,6-diisopropylphenoxide, prepared by addition of 0.036 g (1.50 mmol) of NaH to a solution of 0.237 g (1.33 mmol) of 2,6-diisopropylphenol in 50 mL of THF. Vigorous stirring was continued for 72 h at room temperature. The resulting clear, pale yellow solution was filtered through Celite, and the volatiles were removed *in vacuo* to yield an off-white solid. The solid was washed with 50 mL of hexane, yielding no soluble material. The solid was then extracted into 50 mL of toluene and filtered through a Celite pad. The volume of the filtrate was reduced to 20 mL *in vacuo*, and the flask was then cooled to −40 °C. Clear colorless crystals were deposited overnight. Yield: 1.437 g (99%). ^{1}H NMR (300 MHz, benzene-*d*$_6$): δ 7.08 (d, $J = 7$ Hz, 2 H, *meta* OAr), 6.80 (t, $J = 7$ Hz, 1 H, *para* OAr), 3.58 (br septet, $J = 7$ Hz, 2 H, C*H*Me$_2$), 3.25 (br m, 3 H, α-THF), 1.25 (d, $J = 7$ Hz, 12 H, CH*Me*$_2$), 1.20 (br m, 3 H, *β*-THF). ^{1}H NMR (300 MHz, toluene-*d*$_8$, 193 K): δ 7.14 (br, 2 H, *meta* OAr), 6.94 (br, 1 H, *para* OAr), 3.61 (br, 2 H, C*H*Me$_2$), 3.50 (br m, 1 H, α-THF−La), 2.52 (br m, 2 H, α-THF−Na), 1.30 (br, 12 H, CH*Me*$_2$), 0.86 (br m, 3 H, *β*-THF). IR (cm^{-1}): 1588 (m), 1429 (s), 1378 (m), 1359 (w), 1327 (m), 1279 (sh, w), 1262 (s), 1204 (m), 1141 (w), 1108 (w), 1098 (w), 934 (w), 886 (m), 861 (sh, w), 852 (m), 842 (m), 754 (s), 744 (s), 722 (w), 684 (m). Anal. Calcd for C$_{60}$H$_{92}$LaNaO$_7$ (lattice solvent lost on standing): C, 66.28; H, 8.53. Found: C, 65.92; H, 8.73.

Cs[La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (4). La$_2$(OAr)$_6$ (0.101 g, 0.0753 mmol) was dissolved in toluene (10 mL) in the drybox, and this solution was added to a 3:1 toluene/THF solution (10 mL) of 0.049 g (0.15 mmol) of cesium 2,6-diisopropylphenoxide. Vigorous stirring was continued for 72 h at room temperature. The resulting purple solution was filtered through Celite, and the volatiles were removed *in vacuo* to yield a purple solid. The solid was then extracted into 50 mL of hot toluene and filtered again through Celite. The volume of the filtrate was reduced to 30 mL *in vacuo*, and the flask was then cooled to −40 °C. Overnight a pink powder had deposited. Yield: 0.054 g (37%). ^{1}H NMR (300 MHz, THF-*d*$_8$): δ 6.79 (d, $J = 7$ Hz, 2 H, *meta* OAr), 6.36 (t, $J = 7$ Hz, 1 H, *para* OAr), 3.65 (septet, $J = 7$ Hz, 2 H, C*H*Me$_2$), 1.10 (d, $J = 7$ Hz, 12 H, CH*Me*$_2$). IR (cm^{-1}): 1583 (m), 1426 (s), 1377 (m), 1359 (w), 1335 (m), 1276 (s), 1209 (m), 1156 (w), 1138 (w), 1110 (w), 1104 (w), 1060 (w), 1042 (m), 958 (w), 934 (w), 919 (w), 908 (w), 885 (m), 852 (m), 805 (w), 795 (m), 754 (s), 723 (m), 684 (m), 668 (w), 615 (w), 605 (w), 596 (w), 564 (m), 546 (s). Anal. Calcd for C$_{48}$H$_{68}$CsLaO$_4$: C, 58.78; H, 6.99. Found: C, 59.10; H, 7.10.

Crystallographic Studies. (THF)La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(*μ*-O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$Li(THF) (2). A light yellow, triangular-shaped slab was attached to a thin glass fiber using silicone grease. The crystal was immediately placed under a nitrogen cold-stream on a Siemens P4/PC diffractometer. The radiation employed was graphite monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction (including Lorentz and polarization corrections), structure solution, and graphic procedures used SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELX 93 software.[27] No absorption corrections were performed due to the low (<10 cm^{-1}) absorption coefficient.

The space group *Pbca* was uniquely determined by the systematic absences. Patterson techniques were used to locate the lanthanum atom. The remaining atoms appeared in subsequent Fourier synthesis. All hydrogen atoms were refined using the riding model in the HFIX facility in SHELX 93.[27] The final refinement included anisotropic thermal parameters on all non-hydrogen atoms. Hydrogen atoms had their isotropic temperature factors fixed at 1.2 (ethyl and phenyl) or 1.5 (methyl) times the equivalent isotropic *U* of the carbon atom to which they were bonded. The final refinement converged to R1 = 0.0457 and R2$_w$ = 0.1049.[28]

(THF)La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$(*μ*-O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$Na(THF)$_2$·(C$_7$H$_8$)$_2$ (3). A colorless, triangular-shaped slab was attached to 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 cold stream on a Siemens P4/PC diffractometer. The radiation used was graphite monochromatized Mo Kα radiation ($\lambda = 0.710\,69$ Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction (including Lorentz and polarization corrections), structure solution, and graphic procedures used SHELXTL PC Version

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(27) XSCANS, SHELXTL PC, and SHELXL 93 are products of Siemens Analytical X-ray Instruments, Inc., 6300 Enterprise Lane, Madison, WI 53719.

(28) $R1 = \sigma||F_o| - |F_c||/\sigma|F_o|$ and $R2_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$, with $P = [0.33333(\text{maximum of } 0 \text{ or } F_o^2) + (0.66667)F_c^2]$.

4.2/360 software. The structure refinement was performed using SHELX 93 software. No absorption corrections were performed due to the low ($<$10 cm^{-1}) absorption coefficient.

The space group *Pbca* was uniquely determined by the systematic absences. Patterson techniques were used to locate the lanthanum atom. The remaining atoms appeared in subsequent Fourier synthesis. Two toluene solvent molecules were located in the lattice and refined anisotropically. All hydrogen atoms were refined using the riding model in the HFIX facility in SHELX 93. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms. Hydrogen atoms had their isotropic temperature factors fixed at 1.2 (ethyl and phenyl) or 1.5 (methyl) times the equivalent isotropic *U* of the carbon atom to which they were bonded. The final refinement converged to R1 = 0.0659 and R2$_w$ = 0.1207.[29]

Cs[La(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (4). A colorless slab was attached to a thin glass fiber using silicone grease. The crystal, which was mounted from a pool of mineral oil bathed in argon, turned orange upon rapid transfer to a nitrogen cold stream on a Siemens P4/PC diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.710 69 Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction (including Lorentz and polarization corrections), structure solution, and graphic procedures used SHELXTL PC Version 4.2/360 software. The structure refinement was performed using SHELX 93 software. All data were corrected for absorption using the ellipsoid routine in the XEMP facility of SHELXTL PC.

The space groups *C*2/*c* and *Cc* were suggested by systematic absences. Patterson techniques were used to locate the La and Cs atoms in space group *C*2/*c*. The remaining non-hydrogen atoms appeared in subsequent Fourier synthesis. All hydrogen atoms were fixed and refined using the riding model in the HFIX facility in SHELX 93. Hydrogen atoms had their isotropic temperature factors fixed at 1.2 (aromatic) and 1.5 (methyl) times the equivalent isotropic *U* of the carbon atom they were bonded to. The final refinement included anisotropic thermal parameters on all non-hydrogen atoms and converged to R1 = 0.0358 and R2$_w$ = 0.0757.[30] Attempts to refine the *C*2/*c* Patterson solution in space group *Cc* failed.

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Supporting Information Available: Tables of fractional atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for complexes **2**, **3**, and **4** (31 pages). Ordering information is given on any current masthead page.

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(29) R1 = $\sigma||F_o| - |F_c||/\sigma|F_o|$ and R2$_w$ = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 22.9864P]$, with $P = (F_o^2 + 2F_c^2)/3$.

(30) R1= $\sigma||F_o| - |F_c||/\sigma|F_o|$ and R2$_w$ = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 44.2661P]$, with $P = (F_o^2 + 2F_c^2)/3$.