Inorg. Chem. **2003**, *42*, 6089–6094

Inorganic Chemistry
Article

Synthesis of Group 1 Metal 2,6-Diphenylphenoxide Complexes [M($OC_6H_3Ph_2$-2,6)] (M = Li, Na, K, Rb, Cs) and Structures of the Solvent-Free Complexes [Rb($OC_6H_3Ph_2$-2,6)]$_x$ and [Cs($OC_6H_3Ph_2$-2,6)]$_x$: One-Dimensional Extended Arrays of Metal Aryloxides

Charles S. Weinert,* Phillip E. Fanwick, and Ian P. Rothwell*

Department of Chemistry, Purdue University, 560 Oval Drive,
West Lafayette, Indiana 47907-2084

Received June 12, 2003

Reaction of 2,6-diphenylphenol ($HOC_6H_3Ph_2$-2,6) with ^{n}BuLi, NaH, KH, or Rb or Cs metal in benzene gives the solvent-free complexes [M(OAr)]$_x$ in excellent yield. The complex [Rb($OC_6H_3Ph_2$-2,6)]$_x$ exhibits a ladderlike structure in the solid state with triply bridging oxygen atoms and Rb–O distances of 2.743(3), 2.930(2), and 2.973(2) Å. The Rb cations interact with the π-electron cloud of the arene moieties, giving rise to a high Rb coordination number. The cesium-containing congener forms a layered, columnlike structure consisting of [$Cs_2(\mu_2$-OAr$)_2$] units, with nearly identical Cs–O distances of 2.945(2) and 2.947(2) Å. The individual layers are held together solely by Cs–arene π-interactions.

Introduction

The structural chemistry of group 1 metal complexes has been the focus of much research. The reactivity and structure of these complexes are intimately related, and thus, knowledge of their structures is important for an understanding of their reactivity. These materials are often found as aggregates (dimers, trimers, etc.) in the solid state and in solution, and they exhibit a wide variety of solid-state structures.[1−5] The structure and reactivity of group 1 alkoxide and aryloxide complexes is of interest due to the use of these species as synthons. Their degree of aggregation is in a large part influenced by the steric bulk of the alkoxide or aryloxide group as well as the presence and nature of Lewis base donor molecules.[6] In the case of aryloxide derivatives of the group 1 metals, a large number of structurally characterized lithium[7−28] and sodium-containing[10,19,27,29−41] species have been reported. Substantially fewer potassium-containing derivatives are known,[9,29,34,35,42−44] while even fewer rubidium and cesium aryloxide complexes have been structurally characterized. Examples of these include the picrate complexes [Rb(μ_2-$OC_6H_2(NO_2)_3$-2,4,6)]$_x$ and [Cs(μ_2-$OC_6H_2(NO_2)_3$-2,4,6)]$_x$,[9,10] the racemic binaphthoxide solvates [Rb($OC_{10}H_6C_{10}H_6OH$)]·($HOC_{10}H_6C_{10}H_6OH$) and Cs[$OC_{10}H_6C_{10}H_6OH$]·($HOC_{10}H_6C_{10}H_6OH$),[45] and the phenoxide complex [Cs-

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* To whom correspondence should be addressed. E-mail: rothwell@purdue.edu (I.P.R.); weinert@purdue.edu (C.S.W.).

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10.1021/ic0346580 CCC: $25.00 © 2003 American Chemical Society
Published on Web 08/29/2003

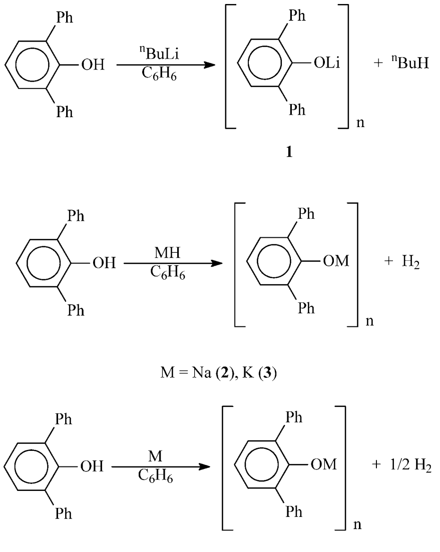
$(OC_6H_3{}^iPr_2$-2,6)$]_x$.[46] The picrate and phenoxide complexes adopt polymeric structures in the solid state.

We recently reported a series of mixed group 1 metal/germanium 2,6-diphenylphenoxide cage complexes [M(μ_2-$OC_6H_3Ph_2$-2,6$)_3$Ge] (M = Li, Na, K, Rb, Cs), which are synthesized from the alkali metal phenoxides [$MOC_6H_3Ph_2$-2,6] and GeI_2.[47] During the course of this study, we prepared the complete series of solvent-free alkali metal 2,6-diphenylphenoxide complexes [$MOC_6H_3Ph_2$-2,6]. We now wish to report the syntheses of these compounds and the structures of the two heaviest congeners, [Rb($OC_6H_3Ph_2$-2,6)$]_x$ and [Cs($OC_6H_3Ph_2$-2,6)$]_x$.

Results and Discussion

Synthesis of Solvent-Free Complexes of [$MOC_6H_3Ph_2$-2,6] (M = Li, Na, K, Rb, Cs). The alkali metal complexes [M($OC_6H_3Ph_2$-2,6)] were prepared via three different routes, as shown in Scheme 1. The reactions were carried out in benzene solvent, and therefore coordinating solvents such as THF or Et_2O are absent from their molecular formula as confirmed by elemental analysis. The lithium complex [Li($OC_6H_4Ph_2$-2,6)] (**1**) was synthesized via reaction of 2,6-diphenylphenol with ^nBuLi in benzene, resulting in formation of butane gas as the side product. Complex **1** is soluble in benzene but can be obtained in the solid form by layering a benzene solution of **1** with hexane, resulting in precipitation of the pure product. We have previously reported the synthesis of **1** in hexane and its use for the preparation of other metal aryloxide species,[48−51] and an etherate of **1** has also been reported and used for the preparation of bis(2,6-diphenylphenoxide) complexes of tungsten[52] and niobium.[53]

Scheme 1



1

M = Na (**2**), K (**3**)

M = Rb (**4**), Cs (**5**)

The sodium and potassium complexes [Na($OC_6H_3Ph_2$-2,6)] (**2**) and [K($OC_6H_3Ph_2$-2,6)] (**3**) were prepared by reaction of the corresponding alkali metal hydride with a benzene solution of 2,6-diphenylphenol. These materials readily precipitate from benzene solution, and use of a slight excess of the phenol allows isolation of pure solid product after washing with hexane and drying *in vacuo*. Rapid evolution of dihydrogen was observed in both cases; gas evolution was observed for a longer period of time in the preparation of **3**, indicating the reaction which yields complex **2** proceeds to completion more rapidly than that for complex **3**. Complex **2** has been previously reported as diethyl ether,[54] THF,[55−58]

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or dioxane[59] solvates and applied to the synthesis of the lanthanoid complexes [Na(Ln{$OC_6H_2Ph_2$-2,6}$_4$] (Ln = Nd or Er).[55,56] Potassium 2,6-diphenylphenoxide has been reported as the THF solvate on three separate occasions.[60−62] Hence, this study represents the first isolation of **2** and **3** as solvent-free complexes.

The rubidium and cesium complexes [Rb($OC_6H_3Ph_2$-2,6)]$_x$ (**4**) and [Cs($OC_6H_3Ph_2$-2,6)]$_x$ (**5**) were obtained via reaction of the pure metal with a benzene solution of the phenol. Neither **4** nor **5** has been previously reported in the literature, although the solvent-free cesium aryloxide complex [Cs-($OC_6H_3Pr^i_2$-2,6)]$_x$ (**6**) is known and has been structurally characterized;[46] it has also been used for the preparation of [Cs_2(La{$OC_6H_3Pr_2^i$-2,6}$_5$].[55] In the syntheses of **4** and **5**, an excess of the phenol was again employed, resulting in complete consumption of the alkali metal after stirring for 18 h. Evolution of dihydrogen was also observed in these reactions, although at a much slower rate than for the syntheses of **2** and **3**. Compounds **4** and **5** readily precipitate from benzene solution which allows for their facile isolation.

Structures of [$RbOC_6H_3Ph_2$-2,6]$_x$ (4) and [$CsOC_6H_3Ph_2$-2,6]$_x$ (5). Compound **4** crystallizes in the space group $P2_1/c$ and forms an extended array of RbOAr groups which assemble in an infinite ladder structure. The structure of **4** consists of a series of planar Rb_2O_2 trapezoid "rungs" which generate an extended ladderlike array via reflection about an inversion center followed by translation of the Rb_2O_2 fragment. Each rubidium atom is bound to three oxygen atoms, and each oxygen atom is connected to three rubidium atoms. An ORTEP diagram illustrating the environment about rubidium is shown in Figure 1, a section of the extended framework is illustrated in Figure 2, and selected bond lengths and angles are summarized in Table 1. The closest Rb−O(1) contact of 2.734(3) Å is in all cases between a rubidium atom and an oxygen atom that comprise a "rung" of the ladder. The Rb−O(1) contact of 2.930(2) Å occurs between Rb and the other oxygen atom of the trapezoid, while the longer Rb−O(1) distance of 2.973(2) Å occurs between Rb and an oxygen atom of an adjacent trapezoid. Both the O(1)−Rb−O(1) and Rb−O(1)−Rb angles along the sides of the ladder are 155.5(1)°. The O(1)−Rb−O(1) angles within a single trapezoid have a value of 96.20(7)°, while the O(1)−Rb−O(1) angles where one of the oxygen atoms belongs to an adjacent trapezoid have a value of 96.50(7)°.

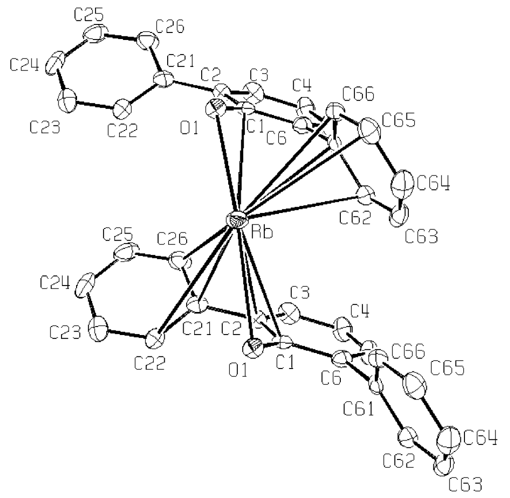

Figure 1. ORTEP diagram of [Rb($OC_6H_3Ph_2$-2,6)]$_x$ (**4**) illustrating the environment about rubidium. Thermal ellipsoids are drawn at 50% probability.

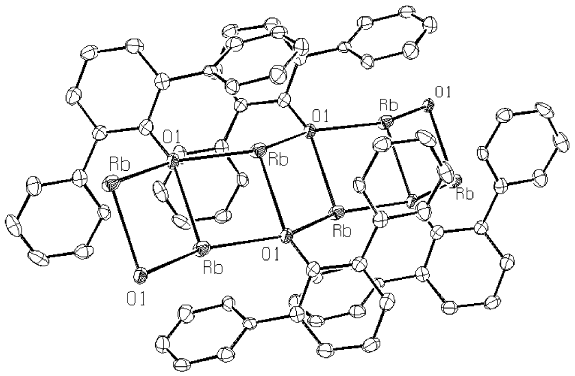

Figure 2. Diagram illustrating a portion of the extended array of **4**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Rb($OC_6H_3Ph_2$-2,6)]$_x$ (**4**)

Rb−O(1)	2.734(3)	Rb−O(1′)	2.930(2)
Rb−O(1″)	2.973(2)	Rb−C(1)	3.183(3)
Rb−C(2)	3.290(4)	Rb−C(1′)	3.632(3)
Rb−C(21)	3.251(4)	Rb−C(22)	3.552(4)
Rb−C(26)	3.637(4)	Rb−C(61′)	3.157(4)
Rb−C(62′)	3.343(4)	Rb−C(65′)	3.674(4)
Rb−C(66′)	3.324(4)		
O(1)−Rb−O(1″)	155.5(1)	Rb−O(1)−Rb′	155.5(1)
O(1)−Rb−O(1′)	96.20(7)	O(1)−Rb−O(1″)	96.50(7)

The rubidium atoms in **4** are coordinated to the carbon atoms of the 2,6-diphenylphenoxide moieties via the π-electron cloud. These interactions occur along the sides of the ladder, but not across the rungs of the ladder. There are two types of interactions: five *intra*trapezoidal contacts between the Rb atom and the carbon atoms on the 2,6-diphenylphenoxide group, and a similar set of five intertrapezoidal contacts. In the intratrapezoidal case, two of these interactions are between Rb and the C atoms of the phenoxide ring, with distances of 3.183(3) Å for the *ipso*-C contact and 3.290(4) Å for the *ortho*-C contact. The remaining three interactions occur between Rb and the C atoms of the *ortho*-phenyl substituents, with distances of 3.251(4), 3.552(4), and 3.637(4) Å for the Rb−C(21), Rb−C(22), and Rb−C(26) contacts. However, for the *inter*trapezoidal interactions only

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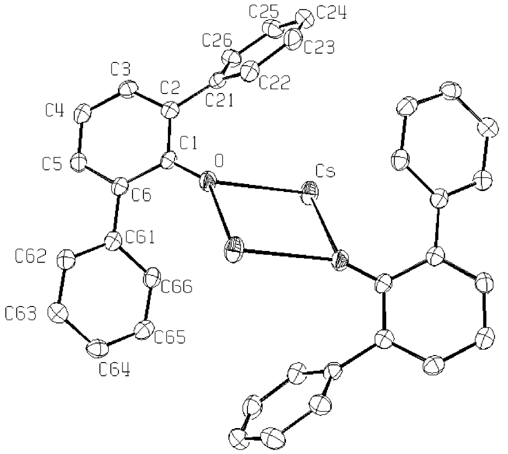

Figure 3. ORTEP diagram of [Cs(OC$_6$H$_3$Ph$_2$-2,6)]$_x$ (**5**) illustrating an individual Cs$_2$(OAr)$_2$ dimeric fragment. Thermal ellipsoids are drawn at 50% probability.

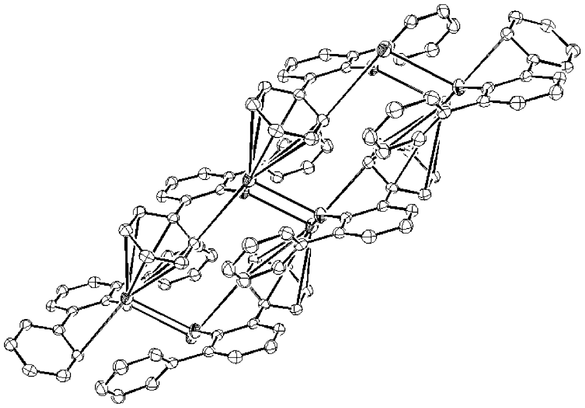

Figure 4. Diagram illustrating the extended array of **5**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Cs(OC$_6$H$_3$Ph$_2$-2,6)]$_x$ (**5**)

Cs−O	2.945(2)	Cs−O	2.947(2)
Cs−C(61)	3.675(3)	Cs−C(62)	3.650(3)
Cs−C(63)	3.677(3)	Cs−C(64)	3.705(3)
Cs−C(65)	3.702(3)	Cs−C(66)	3.704(3)
O−Cs−O′	86.22(5)	Cs−O−Cs′	93.79(5)

one contact with the phenoxide ring is present, with a distance of 3.632(3) Å. There are also four intertrapezoidal distances with an *ortho*-phenyl ring which measure 3.157(4), 3.343(4), 3.674(4), and 3.324(4) Å for the Rb−C(61′), Rb−C(62′), Rb−C(65′), and Rb−C(66′) contacts, respectively. Therefore, the 10 Rb−C close contacts and 3 Rb−O bonds result in a formal coordination number of 13 for rubidium.

Although **4** is the first rubidium/aryloxide system to exhibit an infinite ladderlike structure, a number of similar rubidium-containing complexes contain this structural motif. The structure of the rubidium phosphide complex [Rb(THF)(HPC$_6$H$_2$Pr$^i_3$-2,4,6)]$_x$ (**7**) is very similar to that of **4**.[63] This material consists of a series of Rb$_2$P$_2$ fragments which generates an infinite ladder in the same manner as the Rb$_2$O$_2$ fragments in **4**. However, the ladder structure in **7** is puckered and exhibits P−Rb−P angles of 142.77(4)° and 141.47(4)° and Rb−P−Rb angles of 166.17(5)° and 165.32(6)°. Similar puckered-ladder structures were found for the heavy group 1 metal−phosphide complexes [M(THF)P(SiMe$_3$)$_2$]$_x$ (M = K, Rb, Cs)[64] as well as for [KP(H)Mes*]$_x$ (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$).[65] Complexes of the lighter group 1 metals which exhibit a ladderlike structure are also known, as in [Li(THF)PHCy]$_x$.[66] Additionally, each Rb atom in **7** is η^6-coordinated to the aryl substituent attached to the adjacent phosphorus atom, with Rb−C distances ranging from 3.116(4) to 3.659(6) Å.

Compound **5** also crystallizes in the space group $P2_1/c$ but is not isostructural with **4**. The structure of **5** consists of individual [Cs$_2$(μ_2-OAr)$_2$] fragments which form an extended array via η^6-interactions between the cesium atoms and the *ortho*-phenyl rings on the 2,6-diphenylphenoxide anions of neighboring [Cs$_2$(μ_2-OAr)$_2$] fragments. An ORTEP plot of a [Cs$_2$(μ_2-OAr)$_2$] dimer is shown in Figure 3, and a portion of the extended framework is illustrated in Figure 4. Selected bond distances and angles are summarized in Table 2. The individual [Cs$_2$(μ_2-OAr)$_2$] fragments consist of a planar four-membered ring containing two cesium atoms and two bridging aryloxide groups. The ring contains a crystallographic center of inversion, and therefore, the two cesium atoms are identical, as are the two aryloxide groups. The cesium−oxygen distances of 2.945(2) and 2.947(2) Å are identical within a standard deviation. The two identical Cs−O−Cs angles measure 93.79(5)°, while the O−Cs−O angles are slightly more acute, measuring 86.22(5)°.

The extended structure of **5** can be described as individual [Cs$_2$(μ_2-OAr)$_2$] fragments stacked in a layered fashion. The individual fragments are attached to one another by an alternating up-and-down pattern of Cs-η^6 phenyl interactions. Two of the four *ortho*-phenyl rings within an individual [Cs$_2$(μ_2-OAr)$_2$] fragment participate in these interactions, while the other two remain uncoordinated. Thus, in one individual fragment, the *ortho*-phenyl ring containing C(61)−C(66) is bound to the cesium atom in the layer above, while the symmetry related *ortho*-phenyl ring on the opposite side of the [Cs$_2$(μ_2-OAr)$_2$] trapezoid is bound to the cesium atom in the layer below. The Cs−C distances range from 3.650(3) to 3.705(3) Å, the individual layers are separated by 7.31 Å, and the shortest Cs−O distance between stacked layers is 6.10 Å. Neither of the symmetry-related *ortho*-phenyl rings containing C(21)−C(26) are involved in bonding to cesium.

The cesium aryloxide complex [Cs(OC$_6$H$_3$Pr$^i_2$-2,6)]$_x$ (**6**) was also found to have an extended structure in the solid state.[46] However, in addition to η^6-coordination of the cesium cations to the π-electron cloud of the phenoxide rings, the individual CsOAr fragments are also connected via Cs−O bonds with neighboring fragments and form extended chains via these interactions. The one-dimensional chains are also further assembled into two-dimensional sheets via Cs−C interactions. Thus, this material is not held together solely by π-interactions, as found for **5**. The presence of *ortho*-

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isopropyl groups in **6** rather than *ortho*-phenyl groups likely results in the formation of extended chains of CsOAr units held together by the aryloxide oxygen atoms and π-arene interactions, rather than the layered columnlike array of $[Cs_2(\mu_2\text{-}OAr)_2]$ dimers held together solely by π-interactions found in **5**. Additionally, the increased steric bulk of the phenyl versus the isopropyl groups does not allow arrangement of the individual columns of **5** into extended sheets similar to what is observed in **6**.

The Cs−O bond in **5** measuring 2.945(2) Å is significantly longer than the Cs−O distances of 2.875(4) and 2.898(5) Å in **6**. The Cs−C bond distances in **6** vary from 3.375(6) to 3.711(7) Å for the η^6-interactions within the chains. Three of these Cs−C contacts, with the *para*-carbon, 3.375(6) Å, and the two *meta*-carbons, 3.479(6) and 3.468(6) Å, are significantly shorter than those found in **5**, while the other contacts with the *ipso*- and *ortho*-carbon atoms are similar to those of **5**. The complex $[Cs\{(OH)C_6H_4Bz\text{-}2\}_2(OC_6H_4\text{-}Bz\text{-}2)]$, which exists as an extended structure in the solid state as well, exhibits two η^6-phenyl interactions with the two benzyl groups of the benzylphenol ligands.[67] The average Cs−C contacts for these interactions are 3.66 and 3.65 Å, which are shorter than the average Cs−C distance of 3.69 Å for **5**. The presence of the CH_2 group in $[Cs\{(OH)C_6H_4\text{-}Bz\text{-}2\}_2(OC_6H_4Bz\text{-}2)]$ results in more flexible *ortho*-ligands, and thus, the phenyl groups are able to approach the Cs metal center more closely than in the more rigid complex **5**.

Conclusions

The complete series of solvent-free complexes $[M(OC_6H_3\text{-}Ph_2\text{-}2,6)]$ has been prepared, and the X-ray structures of the rubidium and cesium congeners have been determined. Complexes **4** and **5** represent rare examples of structurally characterized aryloxide complexes of the heaviest alkali metals. The large atomic radii of Rb and Cs allow these elements to form extended structures via π-arene interactions and, in the case of Rb, oxo-bridges. These structural characteristics contrast with the those of the lighter group 1 aryloxide complexes, which often adopt dimeric or trimeric structures, as found for $[Li_3(\mu_2\text{-}OC_6HPh_2\text{-}2,6\text{-}{}^tBu\text{-}3,5)_3]$[21] and $[Li(OC_6H_3{}^tBu_2\text{-}2,6)(THF)]_2$.[24] The structures of **4** and **5** are likely governed the nature of the *ortho*-substituents of the aryloxide anions; the steric bulk of these groups, as well as their ability to enter into π-bonding with the alkali metal centers, plays an important role in the nature of the products.

Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard syringe, Schlenk, and glovebox techniques.[68] *n*-Butyllithium (2.5 M in hexanes), sodium hydride, and potassium hydride (35 wt % suspension in mineral oil) were obtained from Aldrich. The suspension of KH was filtered and washed with hexane before use. Rubidium and cesium metal were purchased from K & K Laboratories, Inc. 2,6-Diphenylphenol was prepared by the literature method.[69]

Table 3. Crystal Data and Data Collection Parameters

	4	**5**
formula	$C_{18}H_{13}ORb$	$C_{18}H_{13}CsO$
fw	330.77	378.21
space Group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	5.7681(2)	11.7492(6)
b, Å	21.1759(8)	7.3061(3)
c, Å	11.4656(5)	16.9160(8)
α, deg	90	90
β, deg	96.764(1)	100.989(2)
γ, deg	90	90
V, Å^3	1390.72(9)	1425.5(1)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.580	1.762
T, K	150.	150.
radiation (wavelength)	Mo Kα (0.71073Å)	Mo Kα (0.71073Å)
R	0.050	0.032
R_w	0.078	0.068

Preparation of $[Li(OC_6H_3Ph_2\text{-}2,6)]$ (1). To a solution of 2,6-diphenylphenol (0.98 g, 4.0 mmol) in benzene (10 mL) was added a 2.5 M solution (hexane) of ${}^nBuLi$ (1.75 mL, 4.37 mmol). The solution was stirred for 3 h, and the volatiles were removed in vacuo to yield a while solid, which was washed with hexane (5 × 5 mL) and dried in vacuo. Yield: 0.92 g (92%). Anal. Calcd for $C_{18}H_{13}LiO$: C, 85.71; H, 5.19. Found: C, 85.62; H, 5.15.

Preparation of $[Na(OC_6H_3Ph_2\text{-}2,6)]$ (2). To a suspension of sodium hydride (0.13 g, 5.4 mmol) in benzene (10 mL) was added a solution of 2,6-diphenylphenol (1.40 g, 5.68 mmol) in benzene (10 mL). The solution was stirred for 3 h, and the volatiles were removed in vacuo, resulting in a white solid. The solid was washed with hexane (3 × 5 mL) and dried in vacuo to yield 0.84 g (58%) of $NaOC_6H_3Ph_2$-2,6. Anal. Calcd for $C_{18}H_{13}NaO$: C, 80.58; H, 4.88. Found: C, 80.50; H, 4.79.

Preparation of [K(OC6H3Ph2-2,6)] (3). To a suspension of potassium hydride (0.060 g, 1.5 mmol) in benzene (10 mL) was added a solution of 2,6-diphenylphenol (0.36 g, 1.5 mmol) in benzene (10 mL). After 12 h, a white suspension was present. The solid was isolated by filtration, washed with benzene (3 × 5 mL) followed by hexane (3 × 5 mL), and dried in vacuo. Yield: 0.34 g (83%). Anal. Calcd for $C_{18}H_{13}KO$: C, 76.02; H, 4.61. Found: C, 76.26; H, 5.02.

Preparation of $[Rb(OC_6H_3Ph_2\text{-}2,6)]$ (4). An ampule containing rubidium metal (1.2 g, 14.0 mmol) was broken into a 500 mL flask in the glovebox. To this was added a solution of 2,6-diphenylphenol (4.80 g, 20.0 mol) in 200 mL of benzene. The mixture was stirred for 12 h resulting in a white suspension. The solid was isolated by filtration, washed with benzene (3 × 10 mL), and dried in vacuo to yield 1.57 g (33%) of $RbOC_6H_3Ph_2$-2,6. Anal. Calcd for $C_{18}H_{13}ORb$: C, 65.36; H, 3.96. Found: 65.16, 3.97.

Preparation of $[Cs(OC_6H_3Ph_2\text{-}2,6)]$ (5). An ampule of cesium metal (1.0 g, 7.5 mmol) was broken into a 500 mL round-bottom flask, and a solution of 2,6-diphenylphenol (14.11 g, 57.2 mmol) in benzene (300 mL) was added. The reaction mixture was stirred for 15 h resulting in a white precipitate. The solid was isolated by filtration, washed with benzene (3 × 10 mL) and hexane (3 × 10 mL), and dried in vacuo to yield 2.58 g (91%) of $CsOC_6H_3Ph_2$-2,6. From the combined filtrate and washes, 10.2 g of 2,6-diphenylphenol was recovered. Anal. Calcd for $C_{18}H_{13}CsO$: C, 57.16; H, 3.46. Found: C, 57.53; H, 3.42.

X-ray Data Collection and Reduction. Crystal data and data collection parameters are contained in Table 3. A suitable crystal

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was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å.) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.[70] An empirical absorption correction using SCALEPACK was applied.[71] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[72] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the International Tables for Crystallography.[73] Refinement was performed on a AlphaServer 2100 using SHELX-97.[74] Crystallographic drawings were done using the program ORTEPIII.[75]

Acknowledgment. This work was supported by a grant from the National Science Foundation (Grant CHE-0078405).

Supporting Information Available: Crystallographic data, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0346580

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