Novel Alkali-Metal Coordination in Phenoxides: Powder Diffraction Results on C_6H_5OM (M = Li, Na, K, Rb, Cs)

R. E. Dinnebier,*[†,‡] Maren Pink,[§,∥] J. Sieler,[§] and P. W. Stephens*[†]

Department of Physics, State University of New York at Stony Brook,
Stony Brook, New York 11794-3800, and Institut für Anorganische Chemie, Universität Leipzig,
04103 Leipzig, Germany

Received November 18, 1996[⊗]

We report the *ab initio* structure solutions of C_6H_5OM (M = K, Rb, Cs) by high-resolution powder X-ray diffraction. The compounds, which are of interest for reactions of the Kolbe−Schmitt type, are isostructural. The crystal structures are orthorhombic, space group $Pna2_1$, $Z = 12$, with lattice parameters (a, b, c in Å) 14.1003(1), 17.9121(1), and 7.16475(1) for the K compound, 14.4166(2), 18.2028(2), and 7.4009(1) for the Rb compound, and 14.8448(2), 18.5070(2), and 7.6306(1) for the Cs compound. They have a chain structure ${}^{1}_{\infty}[M^{[6]}M_2^{[3]}O_3^{[2]}]$ along the crystallographic c axis. This is a very unusual arrangement in which two different alkali-metal coordination spheres are observed: a distorted octahedron and a 3-fold oxygen coordination. In the latter, the 3-fold-coordinated unsaturated alkali metals additionally show weak interactions with phenyl rings. We also give powder patterns for the compounds with M = Li, Na. The former crystallizes in the monoclinic space group $P2_1/a$ with lattice parameters $a = 22.594$ Å, $b = 4.7459$ Å, $c = 10.053$ Å, and $\beta = 97.82°$ with $Z = 8$, but no structure solution was possible. The powder pattern for the Na phenolate is in agreement with the earlier single-crystal structure.

Introduction

The ability of alkali-metal phenolates to transfer and autotransfer CO_2 and to carboxylate activated C−H bonds is widely known. Applied to sodium phenolate, this is an important mechanism for carbon insertion from CO_2, and the well-known Kolbe−Schmitt reaction[1] is the starting point for the manufacture of many pigments, fertilizers, and even such pharmaceuticals as aspirin. This reaction proceeds from sodium phenolate (C_6H_5ONa) to sodium salicylate (o-hydroxybenzoate), in essentially quantitative yield. The extension to heavier alkali metals is thwarted by the fact that the Kolbe−Schmitt reaction leads to a different result, a fact pointed out by Kolbe in 1874.[2] The carboxylation of potassium phenolate results in a mixture consisting of both *o*- and *p*-hydroxybenzoate. A comparison of the carboxylation results of the alkali-metal phenolates shows a strong dependence on the cation involved.[3] Apart from the synthesis of urea, methanol, and cyclic organic carbonates, the Kolbe−Schmitt reaction is one of the few technically used reactions involving the thermodynamically stable and kinetically inert carbon dioxide. Hence, it is very interesting to learn more about the course of this insertion of CO_2 in order to possibly apply the knowledge to other syntheses with CO_2.

Interestingly, despite extensive research efforts, the mechanism of the Kolbe−Schmitt synthesis is still unknown, although many possible pathways have been suggested.[3] Since this carboxylation is a solid-state reaction, it is first of all desirable to know the crystal structures of the participating materials. Up to now, the only known structure in this series is from a single-crystal study of sodium phenolate.[4] Accordingly, we have undertaken a program to learn the structures of the various reactants and products, and eventually the intermediates. Here we report *ab initio* structure determinations of C_6H_5OM (M = K, Rb, Cs) from powder samples. These results are a noteworthy illustration of the power of high-resolution X-ray powder diffraction for solving complicated crystal structures of organic molecules, with (in this case) 24 atoms in general positions in the asymmetric unit.

Experimental Section

Materials. All manipulations of solvents and substances were conducted under an atmosphere of dry argon using standard Schlenk and vacuum techniques. Tetrahydrofuran (THF) and toluene were predried over powdered potassium hydroxide, freshly distilled from sodium benzophenone ketyl, and kept under argon. Phenol was purified and dried by sublimation immediately prior to use at room temperature under reduced pressure (10^{-1} Torr) at a cooling finger. Rubidium (Aldrich, 99.6%) and cesium (Aldrich, 99.95%) were used without further purification.

Lithium and sodium phenolate were prepared according to known procedures.[5,6]

Potassium Phenolate. Cut potassium was covered with toluene, heated until it melted while the mixture was stirred quickly, and then quenched without further stirring. A solution of phenol in toluene was added dropwise over 2 h to the stirred potassium slurry at about 10 °C. After the reaction, the mixture was warmed slowly and stirred for at least 2 h. Toluene was removed via a filter cannula. The precipitate was washed with pentane, filtered off, dried under vacuum (10^{-3} Torr), and stored under argon.

Rubidium and Cesium Phenolates. The metal (Aldrich, 99.9%) was warmed in its ampule. The ampule was cracked in a glovebox (Braun), and the molten metal was tipped into a flask and covered with THF. The reaction was carried out on a vacuum line. A phenol−THF solution was added dropwise. The reaction mixture was cooled while the phenol was added and subsequently refluxed for 2 h and

---

[†] State University of New York at Stony Brook.

[‡] Present address: Lehrstuhl für Kristallographie, Universität Bayreuth, 95440 Bayreuth, Germany.

[§] Universität Leipzig.

[∥] Present address: Universita di Bologna, Dipartimento "G. Ciamician", I-40126 Bologna, Italy.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) Boullard, O.; Leblanc, H.; Bresson, B. In *Ullmanns Encyclopedia of Industrial Chemistry*, 5th ed.; VCH: Weinheim, Germany, 1993; Vol. A23, p 478.

(2) Kolbe, H. *J. Prakt. Chem.* **1874**, *118*, 89.

(3) Lindsey, A. S.; Jeskey, H. *Chem. Rev.* **1957**, *57*, 583.

(4) Sieler, J.; Kunert, M. *Z. Kristallogr. Suppl.* **1993**, *7*, 188. Dinjus, E.; Kunert, M.; Nauck, M.; Sieler, J. *Chem. Ber.*, in press.

(5) Kornblum, N.; Berrigian, P. J.; Le Noble, W. J. *J. Am. Chem. Soc.* **1985**, *85*, 1141.

(6) Berny, M. F.; Perrin, R. *Bull. Soc. Chim. Fr.* **1967**, 1013.

Table 1. Lattice Parameters and Selected Details of Refinements of Alkali-Metal Phenolates[a]

	C_6H_5OLi	C_6H_5ONa	C_6H_5OK	C_6H_5ORb	C_6H_5OCs
a (Å)	22.594(3)	10.3756(1)	14.1003(1)	14.4166(2)	14.8448(2)
b (Å)	4.7459(6)	19.4354(1)	17.9121(1)	18.2028(2)	18.5070(2)
c (Å)	10.053(1)	5.70595(3)	7.16475(2)	7.4009(1)	7.6306(1)
β (deg)	97.82(1)				
V (Å^3)	1067.96(11)	1150.63(1)	1809.58(1)	1942.16(4)	2096.37(5)
V/Z (Å^3)	133.50	143.83	150.80	161.85	174.70
Z	8	8	12	12	12
space group	$P2_1/a$	$Iba2$	$Pna2_1$	$Pna2_1$	$Pna2_1$
calcd density (g/cm^3)	0.622	1.340	1.456	1.832	2.148
R_p		6.42	6.89	6.04	5.74
R_{wp}		8.99	9.16	7.85	8.76
reduced χ^2	14.14 (leBail)	5.13	3.47	6.78	6.70
R_F		8.67	7.69	7.15	8.57
no. of obsd reflns	461	340	855	912	1202
no. of refined params	13 (leBail)	26	50	50	50

[a] R_p, R_{wp}, and R_F refer to the Rietveld criteria of fit for profile, weighted profile, and structure factor, respectively, defined in ref 13.

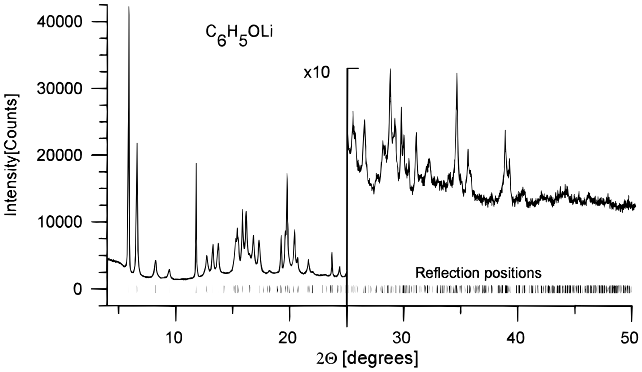

Figure 1. Powder diffraction pattern of C_6H_5OLi at room temperature, with markers at the peak positions indexed by the monoclinic cell listed in Table 1.

stirred at room temperature for an additional 1 h. The solid was filtered off, dried under vacuum (10^{-3} Torr), and kept in a Schlenk vessel under argon.

Powder X-ray Diffraction Experiments. For the powder X-ray diffraction experiments, the air- and moisture-sensitive samples were sealed in glass capillaries of 0.5 and 0.7 mm diameter. High-resolution powder diffraction data were collected at room temperature at the SUNY X3B1 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. X-rays of wavelength 1.15 Å (for C_6H_5OLi, C_6H_5ONa, C_6H_5OK, and C_6H_5ORb) and 0.7 Å (for C_6H_5OCs) were selected by a double Si(111) monochromator. The diffracted beam was analyzed with a Ge(111) crystal and detected with a Na(Tl)I scintillation counter with a pulse height discriminator in the counting chain. The incoming beam was monitored by an ion chamber for normalization for the decay of the storage ring current. Data were taken for 3−8 s at each 2θ step of 0.005−0.02°, depending on the intensity and width of the observed peaks, and all samples were rocked to improve particle counting statistics. Low-angle diffraction peaks from the most crystalline sample, C_6H_5OK, had a width of 0.013° FWHM in 2θ, significantly broader than the resolution of the spectrometer.

The powder patterns are indexed[7] by monoclinic (Li) and orthorhombic (Na, K, Rb, Cs) cells with lattice parameters given in Table 1. Traces of additional phases were present in some of the scans. The space group and number of formula units per unit cell (Z) were found by applying the extinction rules and geometrical considerations. In the case of C_6H_5OLi the crystallinity was so poor that we could not extract sufficient peak intensities to solve the structure, and only the lattice parameters and space group could be determined. Furthermore, there is significant anisotropic broadening of the diffraction lines; i.e., the peak width is not a smooth function of 2θ. Its powder pattern is shown in Figure 1, with peak markers derived from the indexing, and a listing of the integrated intensities in the low-angle part of the spectrum is deposited as Supporting Information. The structure of C_6H_5ONa has recently been solved by single-crystal X-ray diffraction,[4] and the Rietveld refinement of our powder sample, obtained by starting from the single-crystal results, is shown in Figure 2. This comparison provides a useful test for the accuracy of the powder refinements.

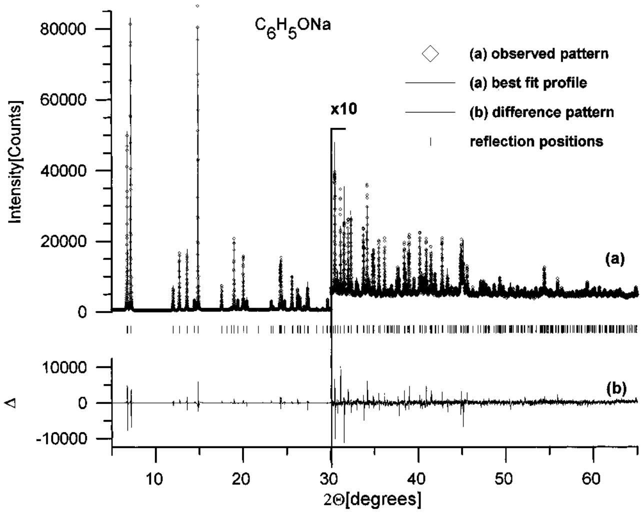

Figure 2. Rietveld plot of orthorhombic C_6H_5ONa at room temperature.

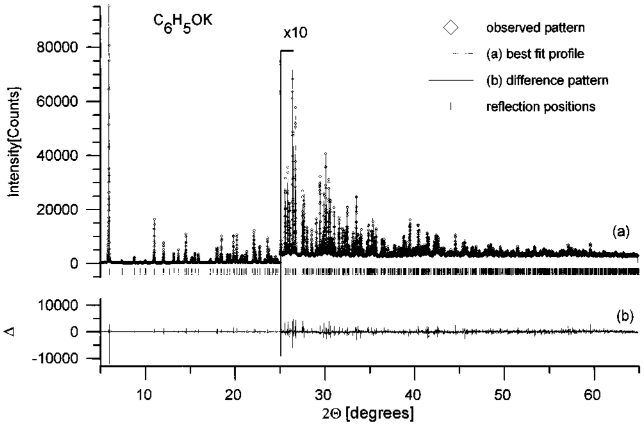

Figure 3. Rietveld plot of orthorhombic C_6H_5OK at room temperature. The asymmetric unit contains 39 atoms (24 non-hydrogen).

In the case of C_6H_5OK, illustrated in Figure 3, about 300 peaks were extracted using the Le Bail technique.[8] These were used as input for the direct-methods program SIRPOW92,[9] with which it was possible to detect the positions of K and some candidate O, but none of the C

---

(7) Visser, J. W. *J. Appl. Crystallogr.* **1969**, *2*, 89.

(8) LeBail, A.; Duryo, H.; Fourquet, J. L. *Mater. Res. Bull.* **1988**, *23*, 447. Rodriguez-Carvajal, J. *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr*, Toulouse, France, 1990; IUCr: Bordeaux, France, 1990; p 127.

Table 2. Selected Bond Distance Ranges and Intramolecular Distances of C_6H_5OA (A = Na, K, Rb, Cs) in Å

	C_6H_5ONa	C_6H_5OK	C_6H_5ORb	C_6H_5OCs
M−M (shortest)	3.16(2)	3.48(2)	3.67(2)	3.929(6)
M−O	2.26(2)−2.37(3)	2.65(6)−2.99(6)	2.8(1)−3.1(1)	3.0(2)−3.3(1)
M−C (shortest)	2.85(2) (asym $\eta^6(\pi)$-interact)	3.07(6) (no interact) 3.09(6) (weak interact)	3.2(1) (no interact) 3.2(1) (weak interact)	3.5(2) (no interact) 3.6(2) (weak interact)
C−O	1.28(2)	1.26(5)−1.32(5)	1.31(11)	1.36(14)
C−C (phenyl)	1.39 (fixed)	1.39 (fixed)	1.39 (fixed)	1.39 (fixed)
C−H (phenyl)	1.06 (fixed)	1.06 (fixed)	1.06 (fixed)	1.06 (fixed)
H−H (shortest interchain)	2.69(2)	2.35(6)	2.4(2)	2.4(5)
O−O (shortest)	3.31(2)	3.49(6)	3.8(1)	3.84(5)

atoms. In the next stage, we searched for the center of gravity locations of the phenyl rings in C_6H_5OK by replacing them with diffuse pseudoatoms having the same number of electrons but a rather high temperature factor. It was possible to Rietveld-refine[10] such structures to Bragg *R* factors of around 30%. After back-substitution of one pseudoatom at a time by the corresponding phenyl ring, grid searches on the rigid-body orientation of the phenyl ring (minimizing the Bragg *R* factor of a subset of about 60 extracted intensities) led to coordinates for all of the non-hydrogen atoms. We used the program package GSAS[11] for the final Rietveld refinements, such as Figures 2 and 3. This package uses the correct formulation of powder peak asymmetry due to axial divergence,[12] which makes a significant (several percent in R_p and R_{wp}) improvement in the quality of the fits. Inclusion of the hydrogens of the phenyl rings reduced the profile *R* factors typically 0.5%. All (non-hydrogen) positional parameters remained within 3σ of the rigid-body positions after turning them loose in a final cycle of refinement. Nevertheless, we have somewhat more confidence in refined values using rigid bodies for the phenyl rings, and so those are the results which are discussed below. C_6H_5ORb and C_6H_5OCs were found to be isostructural. In all cases, isotropic thermal parameters were used. The refined coordinates (using the rigid phenyl ring) are deposited as Supporting Information.

The profile *R* factors listed in Table 1 are somewhat larger than one is used to seeing from conventional powder refinements. This is a consequence of the very high signal to background ratio (300:1) from the high-resolution synchrotron data set and should not be taken as an indication of poor-quality refinements.

The thermal parameters from Rietveld refinements are notoriously inaccurate, especially for absorbing samples in capillaries. They are listed in the Supporting Information for the sake of completeness, but we do not ascribe any significance to their values.

The precision of atomic coordinates derived from powder diffraction experiments has been the topic of extensive discussion.[13] In particular, it is clear that the estimated standard deviations (esd's) derived from the Rietveld least-squares fitting are significantly smaller than any valid measure of the precision of the structural results; it is typically argued that they should be multiplied by a factor of about 3.[13] In this experiment, we can also compare our results to an earlier single-crystal structure of C_6H_5ONa,[4] although it should be noted that crystal was of rather poor quality. The esd's of both sets of atomic coordinates are roughly comparable, and the distribution of differences between the powder and single-crystal refinements is about 6 times broader than the sums of the statistical esd's. This leads to the conclusion that the powder esd's are a factor of 6 smaller than realistic estimates of the precision. Our error estimates in Table 2 and those discussed in the text are the statistical esd's multiplied by this factor of 6.

Results

Since the phenolates of the higher alkali metals are isostructural, we confine ourselves to describe the structure of potassium phenolate. Important bond distances are compared in Table 2.

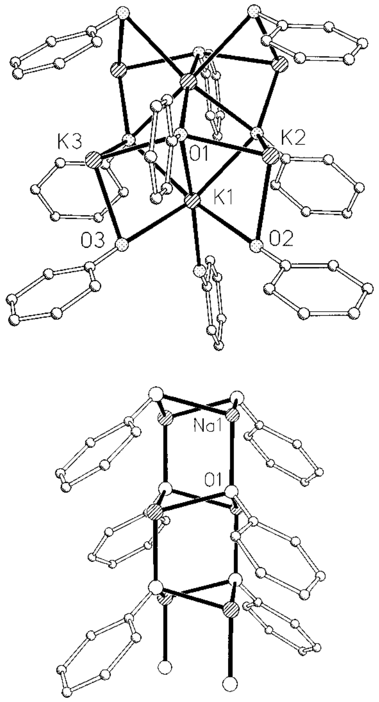

Figure 4. (a, top) Structure of orthorhombic C_6H_5OM (M = K, Rb, Cs). The chain direction is along *c*. (b, bottom) Structure of orthorhombic C_6H_5ONa, from ref 4.

In the unusual structure of C_6H_5OK (Figure 4a), with three formula units on general positions in the asymmetric unit, two different potassium coordination spheres are observed. One potassium ion (K1) is coordinated to six oxygens in a distorted octahedron. These octahedra share faces to form a chain which leads to K−K distances as short as 3.48(2) Å. The other potassium ions are linked to just three oxygens from one octahedron. The 3-fold coordination is a very unusual one for the large alkali-metal cation. Just a few compounds show such a low coordination for a higher alkali metal in an organometallic molecule.[14−16] This structure stands in contrast to C_6H_5ONa (Figure 4b), in which there is only one alkali-metal coordination sphere, containing three oxygens and the carbon atoms of one phenyl ring.

Short distances between potassium and the carbon atoms of the phenyl ring (the shortest is 3.07(6) Å) are observed. This corresponds approximately to the sum of the van der Waals radius of carbon and the ionic radius of potassium.[17,18] The shortest carbon distance to K1 is 3.33(5) Å, but this cannot be regarded as a bond because K1 is 6-fold-coordinated to oxygen

---

(9) Cascarano, G.; Favia, L.; Giacovazzo, C. *J. Appl. Crystallogr.* **1992**, *25*, 310.
(10) Rietveld, H. M. *J. Appl. Crystallogr.* **1969**, *2*, 65.
(11) Larson, A. C.; Von Dreele, R. B. *GSAS*; Report LAUR 86-748; Los Alamos National Laboratory: Los Alamos, NM, 1990.
(12) Finger, L. W.; Cox, D. E.; Jephcoat, A. P. *J. Appl. Crystallogr.* **1994**, *27*, 892.
(13) Langford, J. I.; Louër, D. *Rep. Prog. Phys.* **1996**, *59*, 131.
(14) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 169.
(15) Clarke, P.; Gulbis, J. M.; Lincoln, S. F.; Tiekink, E. R. T. *Inorg. Chem.* **1992**, *31*, 3398.
(16) Chisholm, M. H.; Drake, S. R.; Naiini, A. A.; Streib, W. E. *Polyhedron* **1991**, *10*, 337.
(17) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 2nd ed.; McGraw-Hill: New York, 1977.
(18) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

atoms, and the metal is in an unfavorable position with respect to the p_z orbitals.

Likewise, the short distances between the ipso carbon atoms and K2 and K3 do not indicate a γ interaction, because the potassium is not normal to the phenyl ring. Rather, it is a consequence of the steric hinderance[19] caused by the arrangement of phenyl rings around the chains, which is largely determined by the K−O coordination.

However, both of the outlying potassiums show weak linking to the phenyl ring, indicated by K−C distances between 3.07(6) and 3.34(6) Å to the ortho and meta positions for K2 and, respectively, to the meta and para positions for K3. The distances to the centers of phenyl rings are 3.4(1) Å (K3) and 3.5(1) Å (K2), which are rather long and indicate a very asymmetric and weak interaction. Thus, K2 and K3 must be regarded as coordinatively unsaturated.

Each oxygen atom of the phenolate ions is linked to one carbon and to four potassium ions, with an average distance of 2.77 Å, and so is 5-fold coordinated.

The linking of the coordination polyhedra to form chains is well-known for phenolate−phenol complexes. In this chainlike structure, four out of the eight triangular faces of the octahedron are shared. The apparent mirror plane in the chain with the general formula $^{1}_{\infty}[\mathrm{K}^{[6]}\mathrm{K}_2^{[3]}\mathrm{O}_3^{[2]}]$ makes an angle of about 10° with the unit cell face and is therefore not a symmetry element of the crystal.

Discussion

The uncommon structure of the alkali-metal phenolates explains the high reactivity of the compounds and the strong tendency to include solvents into the structure. The extraordinary low coordination number of the outlying alkali-metal ions and the stress inside the chain, which increases with the ion radius of the cation, explain the behavior toward various reactants.

It is worthwhile to compare the present results to the alkali-metal phenolate−phenol complexes ($C_6H_5OM\cdot nC_6H_5OH$),[20,21] where the phenyl rings are $^6(\gamma)$-coordinated by the alkali metal, the distances to the centers of the phenyl rings are short (2.96 Å for $C_6H_5OK\cdot 2C_6H_5OH$ and 3.16 Å for $C_6H_5OK\cdot 3C_6H_5OH$), and the angle between the normal to the phenyl ring and the cation is close to 0°.

Returning to the Kolbe−Schmitt reaction, speculations concerning the carboxylation results can be drawn from the crystal structures presented. In the structures of the higher alkali-metal phenolates, two out of three of the cations have a low coordination and lie in an accessible position at the outside of the chains. Since it is believed that, in the first step of carboxylation, the metal ion is attacked by CO_2,[22,23] the coordination sphere of the cation and its position in the solid-state structure are of importance. In contrast, the sodium ions in C_6H_5ONa are all 3-fold-coordinated (leaving aside the weak γ interaction) and situated at the edges of the chains. The occurrence of two alkali-metal sites in the higher phenolates could result in the different yields of the ortho and the para products, since the salicylate (ortho form) is obtained from any of the phenolates to some degree. Further investigations of intermediate reaction products are under way, in order to complete the knowledge about the reactants and the mechanism of the carboxylation.

Acknowledgment. Research was carried out in part at the National Synchrotron Light Source at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. The SUNY X3 beamline at NSLS is supported by the Division of Basic Energy Sciences of the U.S. Department of Energy under Grant DE-FG02-86ER45231. Research at the University of Leipzig was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Work at Stony Brook was partially supported by the National Science Foundation Under grant DMR 95-0325.

Supporting Information Available: Listings of low-angle diffraction peak positions and intensities for C_6H_5OLi and atomic coordinates and selected bond distances and angles for the other compounds (9 pages). Ordering information is given on any current masthead page.

IC961385I

---

(19) Pieper, U.; Stalke, D. *Organometallics* **1993**, *12,* 1201.

(20) Stephens, P. W.; Dinnebier, R. E.; Norby, P.; Pink, M; Sieler, J. Powder Diffraction Structure of $C_6H_5OK\cdot 2C_6H_5OH$. *Book of Abstracts*; American Crystallographic Association Meeting, Montreal, Canada, 1995; American Crystallographic Association: Storrs, CT, 1995.

(21) Pink, M.; Sieler, J. *Z. Kristallogr. Suppl.* **1995**, 351.

(22) Hales, J. L.; Jones, J. I.; Lindsey, A. S. *J. Chem. Soc.* **1954**, 3145.

(23) Kunert, M. Dissertation, Universität Jena, 1996.