Lewis Base-Free Phenyllithium: Determination of the Solid-State Structure by Synchrotron Powder Diffraction

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Abstract: The solid-state structure of unsolvated, Lewis base-free phenyllithium (LiC_6H_5) is reported. Structure determination of the simplest lithium aryl was performed by high-resolution synchrotron X-ray powder diffraction. The structure was solved by ab initio methods in combination with difference Fourier analysis and consecutive Rietveld refinements. Solid phenyllithium consists of dimeric Li_2Ph_2 molecules, which strongly interact with adjacent Li_2Ph_2 moieties, forming a polymeric, infinite-ladder structure along the crystallographic *b*-axis. In the Li_2Ph_2 units the two lithium atoms and the C(*ipso*) atoms of the two phenyl rings form an absolutely planar, four-membered ring with the two phenyl rings perpendicular to it. The bonding of the C(*ipso*) atom to the two Li atoms can be described as a three-center, two-electron bond (Li−C 2.24(1) and 2.32(1) Å; Li−C−Li′ 63.2(7)°). The π-electrons of the phenyl rings interact strongly with the lithium atoms of neighboring Li_2Ph_2 moieties.

Introduction

Lithium organic compounds are some of the most extensively investigated compounds in main group organometallic chemistry because of their many applications in research laboratories and industry.[1−3] In addition, the investigation of solid-state structures is important for our understanding of chemical bonding. Over 90% of the known studies of solid-state structures in this field were carried out on Lewis base adducts with nitrogen-, oxygen-, or sulfur containing ligands.[4] Only a few examples of base-free lithium organic compounds, i.e., $[LiEt]_4$,[5] $[Li^nBu]_6$,[6] or $[LiC(SiMe_3)_3]_2$,[7] have been investigated by X-ray single crystal diffraction methods. Lithium organic compounds are often not soluble in noncoordinating solvents, which makes it nearly impossible to obtain base-free single crystals of sufficient size. In some cases the solid-state structures could be determined by X-ray powder diffraction methods, i.e., for $[LiMe]_4$[8] or $[LiCp]_n$.[9] The same problems exists for aryllithium compounds, as was discussed in the literature.[10] The only compounds containing LiPh for which the solid state structure was previously determined are its base adducts: [LiPh(pmdta)][11] (monomer), $[LiPh(tmeda)]_2$[12] (dimer), $[LiPh(Et_2O)]_4$,[13] and $[LiPh(Me_2S)]_4$[14] (both tetramer) (pmdta = pentamethyldiethylenetriamine; tmeda = tetramethylethylenediamine). Recently, Power et al. published a structural model for unsolvated phenyllithium in the solid state, based on the single-crystal structures of four lithium aryl derivatives wherein the phenyl rings are substituted by bulky groups in the *meta* and *para* positions.[10] Here we report the solid-state structure of the simplest lithium aryl, using high-resolution synchrotron X-ray powder diffraction methods.

Results and Discussion

The solid-state structure of base-free phenyllithium consists of the dimeric molecule, Li_2Ph_2, as its fundamental unit (Figure 1). The two Li atoms and the C(*ipso*) atoms of the two phenyl rings form a Li_2C_2 four-membered ring. This ring is absolutely planar because of a crystallographic inversion center in the middle of the ring. The phenyl ring planes are perpendicular to the Li_2C_2 ring plane (90.1°), with the center of the phenyl ring a little (0.073 Å) below the Li_2C_2 plane. The π-electrons of the phenyl rings interact strongly with the lithium atoms of neighboring Li_2Ph_2 moieties. As a result, the phenyllithium crystallizes as a polymeric, infinite-zigzag ladder along the crystallographic *b*-axis. Neighboring, parallel-arranged ladders do not show any interactions with each other. The two Li−C distances within the Li_2C_2 ring are slightly different (Li−C(1)

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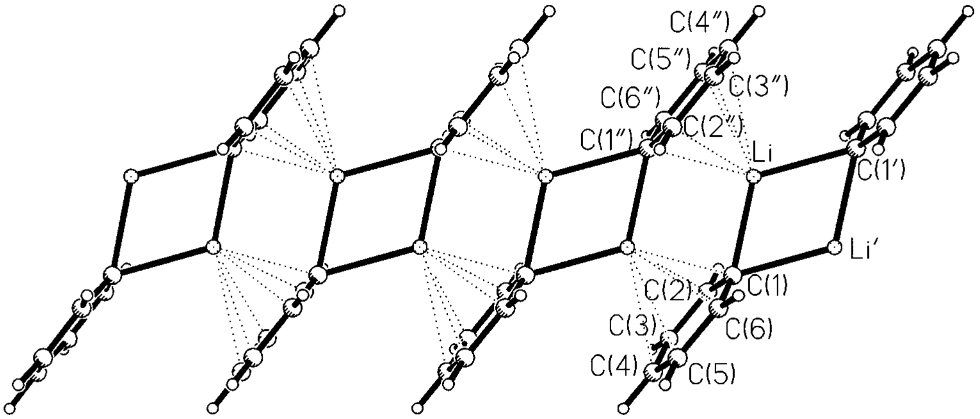
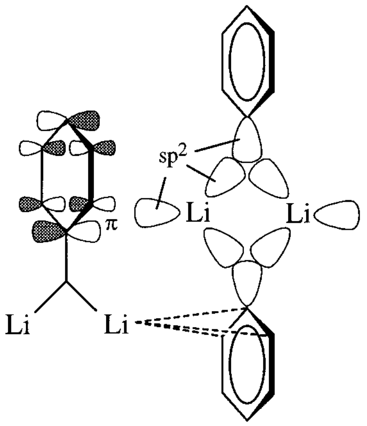


Figure 1. Ball and stick drawing of LiC$_6$H$_5$ (four (LiC$_6$H$_5$)$_2$ units shown).

Chart 1



2.242(14) Å, Li−C(1)′ 2.322(14) Å), the Li−Li′ distance is 2.39(3) Å. Although modern calculations show us that the bonds in lithium organic compounds are 80−88% ionic,[24] the interaction of the C(*ipso*) atom to the two lithium atoms within the Li$_2$C$_2$ ring can be described as a three-center, two-electron bond (3c2e) where the filled sp^2 hybrid orbital of the C(1) of the phenyl anion overlaps with an empty sp^2 hybrid orbital located on each Li$^+$ cation, respectively (Chart 1). This bonding description is consistent with the small Li−C(1)−Li′ angle of only 63.2(7)° and an C(1)−Li−C(1)′ angle of 116.8(7)°. Thus two of the three empty sp^2 hybrid orbitals on each lithium atom are involved in the two 3c2e bonds within the Li$_2$C$_2$ ring. The third sp^2 orbital of the Li atom interacts with the lobe of a filled π-orbital (one of the two HOMO's of the benzene π-system) from an adjacent phenyl ring. Therefore close contacts of the Li atom to the C(*ipso*) atom and to the two C(*ortho*) atoms are found (Li−C(1)″ 2.401(12) Å, Li−C(2)″ 2.514(14) Å, and Li−C(6)″ 2.534(14) Å). The distances to the remaining *meta* and *para* carbon atoms in the phenyl ring (C(3)″, C(5)″, and C(4)″) are rather long (2.745(15) to 2.862(14) Å).

The type of structure found for phenyllithium is completely new in organometallic lithium chemistry. While unsolvated lithium alkyls form tetrameric or hexameric molecules, dimeric units strongly aggregated to a one-dimensional polymeric ladder structure are observed in solid phenyllithium. Knowing this structure, it is now clear why phenyllithium is not soluble in unsolvating hydrocarbon solvents. Only coordinating Lewis bases containing oxygen, sulfur, or nitrogen atoms are able to cleave the polymeric ladder structure by breaking the bonds of the lithium atoms to the π-electron system of the adjacent phenyl rings. It was described in previous literature that phenyllitium interacts with the donor ligands Et$_2$O and Me$_2$S to form the tetrameric complexes [LiPh(Et$_2$O)]$_4$[13] and [LiPh(Me$_2$S)]$_4$[14] of the heterocubane type and that the reaction with the bidentate ligand TMEDA leads to the dimeric compound [LiPh(tmeda)]$_2$,[12] with the tridentate ligand PMDTA forming the monomeric complex [LiPh(pmdta)].[11] The type of bonding found for the phenyl anion is always different for these types of structures. In [LiPh(Et$_2$O)]$_4$ and [LiPh(Me$_2$S)]$_4$ the phenyl anion forms 4c2e σ-bonds to three Li atoms (Li−C bond lengths in the range of 2.277(5) to 2.348(5) Å (Et$_2$O adduct) and 2.234(5) to 2.308(6) Å (Me$_2$S adduct)). The basic structure of the complex [LiPh(tmeda)]$_2$ is quite similar to the structure of base-free LiPh. A planar Li$_2$C$_2$ ring is observed as well. Each Li atom is further coordinated by two N atoms of the TMEDA ligand, thus forming a distorted tetrahedral geometry around the lithium. The bond lengths within the Li$_2$C$_2$ ring are significantly shortened compared to the LiPh. The shortening of the Li−C bonds in the TMEDA adduct can be explained by a stronger 3c2e bond because the phenyl ring is only bound to two Li atoms instead of the three found in LiPh. In the monomeric complex [LiPh(pmdta)], the phenyl anion is bound by the usual 2c2e σ-bond. Therefore a Li−C distance of only 2.135(16) Å is found; this is the shortest observed distance for an unsubstituted phenyl group yet observed. A dimeric unit [LiPh]$_2$ is also observed in many structures of aryllithium compounds with substituted phenyl rings, unsolvated or with Lewis bases (i.e.[LiMes(thf)$_2$]$_2$[15] (Mes = Mesityl), [LiC$_6$H$_3$Mes$_2$]$_2$[16] or [LiC$_6$H$_3$(OMe)$_2$]$_2$).[17]

It is worth mentioning that a few months ago Power et al. suggested hexameric units for uncomplexed LiPh in analogy to the solid-state structure of [LiC$_6$H$_3$-3,5-^{t}Bu$_2$]$_6$.[10] The conclusions in this work were based on the similarity of the ipso carbon ^{13}C NMR chemical shifts. Although the authors did not

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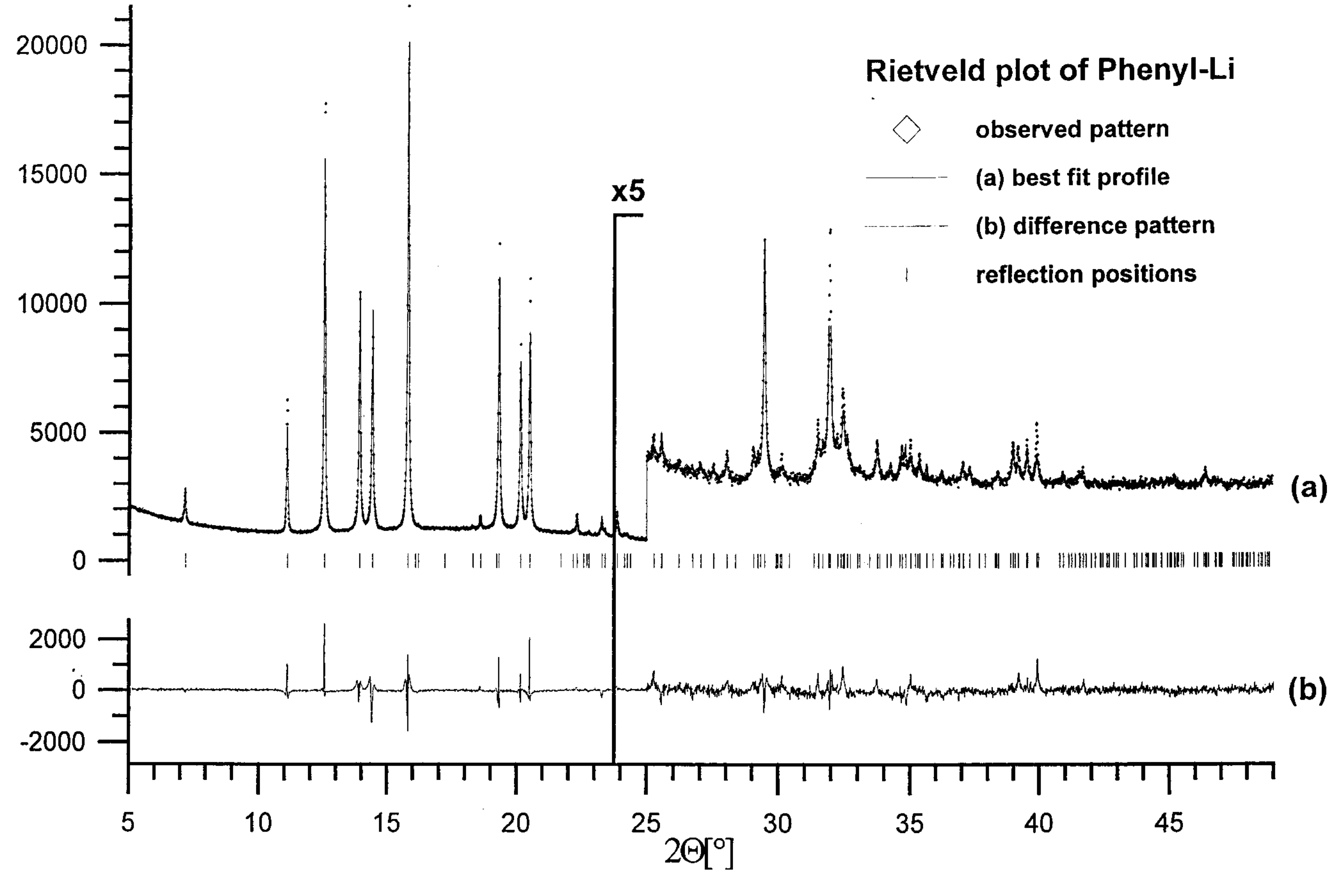

Figure 2. Rietveld plot of LiC_6H_5.

preclude that the insolubility of LiPh in apolar solvents is best attributed to strong intermolecular interactions between $[LiPh]_2$ dimers that stack continuously to give a polymer, which was proposed by van Koten,[18] our work shows now that van Koten was right with the suggestion of a polymer structure for base-free phenyllithium.

Experimental Section

General Procedures. All manipulations were carried out under purified Argon (oxy-sorb-equipment), using standard Schlenk and vacuum techniques. The solvents were heated with Na/K alloy until a blue reaction with benzophenone was observed, than destilled and stored under argon.

Preparation of LiC_6H_5. Phenyllithium was prepared as described in the literature.[19] To obtain a very pure, microcrystalline powder, the compound was recrystallized in the following way (the recrystallization has to be done quickly because of ether cleavage): Phenyllithium (0.69 g, 8.2 mmol) was dissolved at room temperature in diethyl ether (12 mL) and filtered and then the solvent was removed in a vacuum until a white solid precipitated. Cyclopentane (20 mL) was added, the mixture was filtered again, and the precipitate was washed with cyclopentane twice. The product was dried at 10^{-2} Torr. Yield: 0.16 g (23%) of white, pyrophoric powder. IR, ^{1}H NMR, and C,H analysis were carried out to check for remaining diethyl ether in the product.

Crystallographic Procedure. The air and moisture sensitive samples were sealed under argon in glass capillaries of 0.7 mm diameter for the X-ray diffraction experiment. High-resolution powder diffraction data were collected at the SUNY X3B1 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. X-rays of wavelength 1.14966(2) Å were selected by a double Si(111) monochromator. Data were collected at room temperature from $5° < 2\Theta < 49°$. Low-angle diffraction peaks had a fwhm of 0.047° (2Θ). Data reduction was performed with the program GUFI.[20] Indexing with the ITO[21] method yielded the crystallographic data shown in Table 1. The structure was solved by direct methods (program SIRPOW92)[22] in combination with consecutive Rietveld refinements and difference Fourier analysis (program package GSAS).[23] All atoms were refined with isotropic temperature factors. The C−C distances in the phenyl ring (1.391(2) Å) were refined with the same length (not fixed, rigid body model) and the H atoms were calculated in idealized positions

Table 1. Crystallographic Data for LiC_6H_5

formula	C_6H_5Li
fw (g mol^{-1})	84.05
cryst syst	monoclinic
space group	$P2_1/n$
temp (K)	293
cell parameters	
a (Å)	11.528(1)
b (Å)	4.555(1)
c (Å)	10.406(1)
β (deg)	114.24(1)
V (Å^3)	498.22(2)
Z	4
density (calcd g cm^{-3})	1.121
λ (Å)	1.14966(2)
R-values	
R_{wp}	0.0468
R_p	0.0322
R_{F2}	0.0855

Table 2. Fractional Atomic Coordinates and Isotropic Temperature Factors (×100) for LiC_6H_5

atom	*X*	*Y*	*Z*	$(U_i/U_e) \times 100$
Li	0.5063(18)	−0.3026(32)	−0.0726(17)	17.4(7)
C1	0.4932(7)	−0.2063(10)	0.1323(5)	4.48(32)
C2	0.3731(5)	−0.1162(14)	0.1173(3)	7.67(16)
C3	0.3606(4)	0.0735(14)	0.2156(6)	7.67(16)
C4	0.4682(7)	0.1731(10)	0.3289(4)	7.67(16)
C5	0.5884(4)	0.0829(14)	0.3439(4)	7.67(16)
C6	0.6009(4)	−0.1067(14)	0.2456(7)	7.67(16)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for LiC$_6$H$_5$

Li−C1	2.242(14)	Li−C1′	2.322(14)	Li−C1″	2.401(12)
Li−C2″	2.514(14)	Li−C3″	2.745(15)	Li−C4″	2.862(14)
Li−C5″	2.763(15)	Li−C6″	2.534(14)	C−C	1.391(2)
C1−Li−C1′	116.8(7)	C1−Li−C1″	93.8(6)	C1′-Li−C1″	149.3(8)
Li−C1−Li′	63.2(7)	Li−C1−Li″	86.2(6)	Li′-C1−Li″	149.3(8)

(C−H distance 1.05 Å). Crystallographic data, atomic coordinates with isotropic thermal parameters, and bond lengths and angles are given in Tables 1−3. Figure 1 shows a “ball-and-stick” drawing of the molecule; Figure 2 provides a plot of the final Rietveld refinement.

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Supporting Information Available: Crystallographic details and fractional atomic coordinates including hydrogen positions, isotropic thermal parameters, full bond lengths and angles (10 pages). See any current masthead page for ordering and Internet access instructions.

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