

Synthesis and Characterization of Lewis Base-Free, σ -Bonded Lithium Aryls: A Structural Model for Unsolvated Phenyllithium in the Solid State

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Abstract: The synthesis and characterization of four Lewis base-free, σ -bonded lithium aryls are reported. This work was undertaken in order to provide a model for the solid-state structure of phenyllithium, which is currently unknown. Nondonor hydrocarbon solubility of the four lithium aryls ($\text{LiC}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2$) (**1**), ($\text{LiC}_6\text{H}_4\text{-4-}t\text{-Bu}$) (**2**), ($\text{LiC}_6\text{H}_4\text{-4-}n\text{-Bu}$) (**3**), and $\{\text{LiC}_6\text{H}_4\text{-4-SiMe}_2(t\text{-Bu})\}_n$ (**4**) was achieved by the incorporation of *meta*- or *para*-substituents on the aryl rings. This permitted ^{13}C NMR spectroscopy and crystal growth using their solutions. It is proposed that the absence of bulky *ortho*-substituents allows association of the lithium aryls to occur in a manner similar to that of phenyllithium itself. The ^{13}C NMR data for the *ipso*-carbon atoms suggest an association number of at least four or, more probably, six in solution. These data are in agreement with the X-ray crystal structure of **1**, which is hexameric, with a distorted octahedral (trigonal antiprismatic) array of lithium ions. Six of the eight Li_3 faces are capped by an aryl group that interacts primarily through the *C(ipso)* atom. Weaker Li-C(ortho) interactions are also apparent. This structure is the first of this type for an unsolvated, σ -bonded lithium aryl. Crystal data with $\text{Cu K}\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation for **1** at 130 K: **1**, $\text{C}_{84}\text{H}_{126}\text{Li}_6$, $M = 1177.49$, $a = 13.516(2) \text{ \AA}$, $b = 15.124(3) \text{ \AA}$, $c = 20.958(3) \text{ \AA}$, $\alpha = 84.084(13)^\circ$, $\beta = 86.249(11)^\circ$, $\gamma = 68.675(13)^\circ$, $V = 3967.7(11) \text{ \AA}^3$, $Z = 2$, space group $P1$, $R_1 = 0.085$ for 7983 ($I > 2\sigma(I)$) data.

Introduction

The structures of unsolvated, σ -bonded lithium aryls are not as well investigated as their alkyl counterparts.¹ For example, full details of the solid-state structure of the simplest lithium aryl, i.e. LiPh , remain unavailable. Part of the reason for this is the lack of hydrocarbon solubility and low volatility of simple derivatives such as LiPh , $\text{LiC}_6\text{H}_4\text{-4-Me}$, or LiMes ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2^-$), which makes the growth of crystals suitable for X-ray crystallography problematical in the absence of donor solvents such as ethers or amines. Hydrocarbon solubility and consequent ease of crystal growth may be increased by using lipophilic aryl ring substituents, and this has allowed the crystal structures of the unsolvated σ -bonded aryl lithiums (LiTrip)₄² ($\text{Trip} = 2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2^-$), ($\text{LiC}_6\text{H}_3\text{-2,6-Mes}_2$)₂², and ($\text{LiC}_6\text{H}_3\text{-2,6-Dipp}_2$)₂³ ($\text{Dipp} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3^-$) to be determined. These are illustrated in Figure 1. In addition, the structure of a weakly complexed benzene adduct, $\eta^6\text{-C}_6\text{H}_6\cdot\text{LiC}_6\text{H}_3\text{-2,6-Trip}_2$, which has a unique, unassociated structure, is known.³ A characteristic feature of the structures of these sterically crowded lithium aryls is that the Li^+ ion, in addition to being σ -bonded to a phenyl ring, is also π -complexed, either inter- or intramolecularly, by nearby aryl ring(s). Thus, the structure of (LiTrip)₄ is a tetramer (structure **A**, Figure 1) in which the four Li^+ ions lie approximately in a plane, and each Li^+ is σ -bound to one aryl and π -bonded to an aryl ring from a neighboring molecule

within the tetramer. The dimers ($\text{LiC}_6\text{H}_3\text{-2,6-Mes}_2$)₂ (**B**) and ($\text{LiC}_6\text{H}_3\text{-2,6-Dipp}_2$)₂ (**C**) display different types of π -bonding to *ortho*-aryl substituents of the terphenyl ligands.

The observation of π -complexation of the Li^+ ion in these^{2,3} and related⁴ sterically encumbered lithium aryls suggests that π -interactions of this type might be a common feature of σ -bonded lithium aryl structures in general. This hypothesis, however, has received little support from ^{13}C NMR spectroscopy.^{5,6} Thus, Lewis base-free LiPh in the solid state displays a *C(ipso)* chemical shift^{5a} that is very close to that of LiPh in Et_2O solution which, by previous NMR spectroscopic studies,^{6d} was shown to have a structure very similar to that of the tetramer ($\text{Et}_2\text{O}\cdot\text{LiPh}$)₄ in the crystal phase.⁷ The X-ray crystal structure of the latter reveals no $\text{Li}^+\text{-}\pi$ -aryl ring interactions and has a distorted cubane arrangement of four tetrahedrally disposed, ether-solvated Li^+ ions and four σ -bonded phenyls, which triply bridge the Li_3 faces through a *C(ipso)* atom.⁷ In contrast, exact details of the Lewis base-free LiPh structure in the solid state are not currently available.

To investigate the solid-state structure of uncomplexed LiPh , four lithium aryl derivatives, which have hydrocarbon-solubilizing substituents only at the *meta*- or *para*-positions of the phenyl ring, have been synthesized. The absence of bulky substituents at the *ortho*-positions was expected to allow

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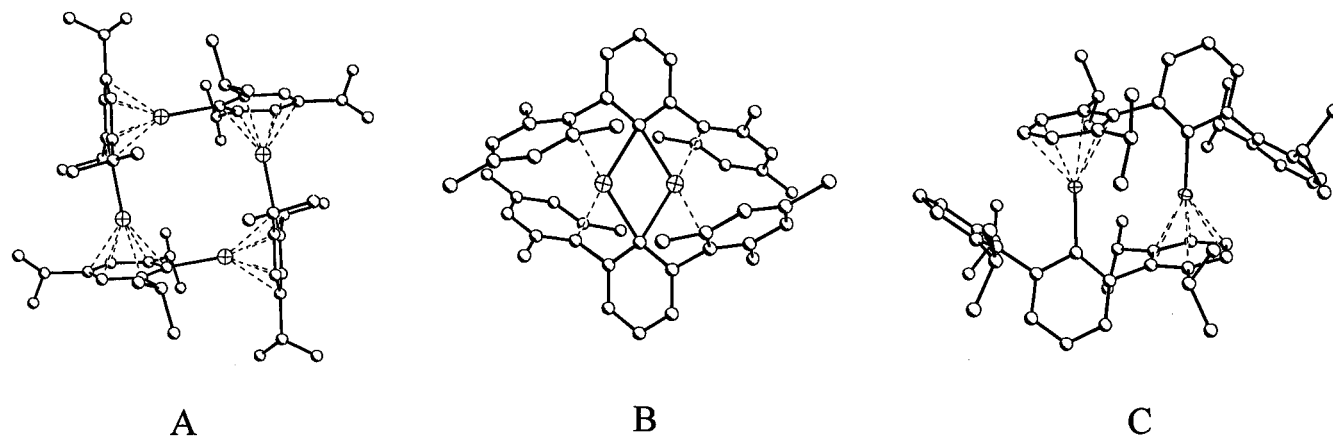


Figure 1. Schematic drawings of the currently known unsolvated lithium aryls $(\text{LiTrip})_4$ (A), $(\text{LiC}_6\text{H}_3\text{-2,6-Mes}_2)_2$ (B), and $(\text{LiC}_6\text{H}_3\text{-2,6-Dipp}_2)_2$ (C). Carbon atoms are shown as circles, lithium atoms as thermal ellipsoids (30%), and σ -bonds as solid lines. Hydrogen atoms are not shown.

association of the lithium aryls to occur in a manner similar to that in phenyllithium itself, while lipophilic substituents at the *meta*- or *para*-positions should provide sufficient hydrocarbon solubility for solution spectroscopy and crystal growth from their solutions. The results of these experiments are now reported.

Experimental Details

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N_2 or in a Vacuum Atmospheres HE43-2 drybox. Solvents were freshly distilled under N_2 from Na/K or Na/K /benzophenone ketyl and degassed twice before use. NMR spectra were obtained on a General Electric QE-300 NMR spectrometer and referenced to an internal standard. ^7Li NMR spectra were referenced to the external standard LiCl in D_2O solution. $\text{Li}(t\text{-Bu})$ (1.5 M) in pentane, 4-*n*- $\text{BuC}_6\text{H}_4\text{Br}$, 4-*t*- $\text{BuC}_6\text{H}_4\text{Br}$, 1,4-dibromobenzene, and *t*- BuMe_2SiCl were purchased commercially and used as received. 3,5-*t*- $\text{BuC}_6\text{H}_3\text{Br}$ was synthesized by a literature procedure.^{8a} 4-*t*- $\text{BuMe}_2\text{SiC}_6\text{H}_4\text{Br}$ was synthesized in a manner similar to 4- $\text{Ph}_3\text{SiC}_6\text{H}_4\text{Br}$,^{8b} by the reaction of *t*- BuMe_2SiCl with $\text{LiC}_6\text{H}_4\text{-4-Br}$, and purified by distillation under reduced pressure (bp 67–69 °C, 0.1 Torr, 59% yield).

$(\text{LiC}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2)_6$ (1). A solution of $\text{Li}(t\text{-Bu})$ (9.4 mmol) in benzene (20 mL) was added dropwise to a solution of 3,5-*t*- $\text{Bu}_2\text{C}_6\text{H}_3\text{-Br}$ (1.28 g, 4.7 mmol) in benzene (30 mL) at room temperature. This produced slight warming, and a very fine white solid began to precipitate from the colorless solution after *ca.* 30 min. After being stirred for 3 days, the precipitate was allowed to settle, and the colorless, slightly cloudy supernatant solution was decanted and was concentrated to *ca.* 30–40 mL. Cooling in a 6 °C refrigerator for 1 week gave 0.15 g of **1** as large (1–2 mm) colorless prisms, which were suitable for X-ray crystallography. Concentration of the mother liquor to *ca.* 5 mL followed by cooling in a 6 °C refrigerator for 4 days gave a further 0.06 g of $(\text{LiC}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2)_6$. Yield: 22.8%. Mp: softens at *ca.* 127 °C and gradually darkens from orange (*ca.* 195 °C) to black (*ca.* 290 °C). No melting was observed below 310 °C. Anal. Calcd for $\text{Li}_{14}\text{H}_{21}$: C, 85.68, H, 10.79. Found: C, 85.90, H, 10.10. ^1H NMR (C_6D_6 , 23 °C): 7.84 (s, *o*-H, 2H), 7.50 (s, *p*-H, 1H), 1.28 (s, *m*- $\text{C}(\text{CH}_3)_3$, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 23 °C): 170.6 (broad, *i*-C), 150.7 (*p*-C), 132.7 (*o*-C), 122.1 (*m*-C), 35.0 (*m*- $\text{C}(\text{CH}_3)_3$), 31.8 (*m*- $\text{C}(\text{CH}_3)_3$). ^7Li NMR (C_6D_6 , 23 °C): 3.5 (s).

$(\text{Et}_2\text{O}\cdot\text{LiC}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2)_4$. Et_2O (13.6 μL , 0.13 mmol, 9.6 mg) was added to **1** (0.025 g, 0.022 mmol) in *ca.* 0.4 mL of C_6D_6 in an NMR tube at room temperature. After *ca.* 15 min, a clear, colorless solution resulted. The NMR spectra taken 15 or 60 min after Et_2O addition were identical. ^1H -NMR: 8.26 (s, broad, *o*-H), 7.45 (s, *p*-H), 2.86 (*q*, OCH_2), $^3J_{\text{HH}} = 6.9$ Hz, 1.50 (s, $\text{C}(\text{CH}_3)_3$), 0.57 (t, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: 171.1 (*i*-C), 147.9 (*p*-C), 133.4 (*o*-C), 120.3 (*m*-C), 65.2 (OCH_2), 34.9 ($\text{C}(\text{CH}_3)_3$), 32.1 ($\text{C}(\text{CH}_3)_3$), 14.2 (OCH_2CH_3). The NMR

data after addition of a second equivalent Et_2O *ca.* 1.5 h later: 8.26 (s, *o*-H), 7.41 (s, *p*-H), 3.08 (*q*, OCH_2), $^3J_{\text{HH}} = 6.9$ Hz, 1.50 (s, $\text{C}(\text{CH}_3)_3$), 0.85 (t, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: 171.8 (*i*-C), 147.5 (*p*-C), 133.8 (*o*-C), 120.2 (*m*-C), 65.6 (OCH_2), 34.9 ($\text{C}(\text{CH}_3)_3$), 32.2 ($\text{C}(\text{CH}_3)_3$), 14.9 (OCH_2CH_3). ^7Li NMR: 2.20. Et_2O in C_6D_6 for comparison: ^1H NMR: 3.25 (*q*, OCH_2), $^3J_{\text{HH}} = 6.9$ Hz, 1.11 (t, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: 65.9 (OCH_2), 15.5 (CH_3).

$(\text{THF}\cdot\text{LiC}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2)_4$. Tetrahydrofuran (14.4 μL , 0.18 mmol, 12.8 mg) was added to a slurry of **1** (0.035 g, 0.03 mmol) in *ca.* 0.4 mL of C_6D_6 at room temperature to give a clear, colorless solution. Further equivalents of THF were added such that the ratios of $\text{Li}:\text{THF}$ were 1:2, 3, 5, and 10. NMR spectra were recorded in each case. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded within 60 min of each THF addition. These spectra are illustrated in Figure 5 (*vide infra*). ^1H NMR: 8.29 (s, *o*-H), 7.43 (s, *p*-H), 3.12 (m, OCH_2), 1.52 (s, *m*- $\text{C}(\text{CH}_3)_3$), 1.11 (m, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR: 173.4 (*i*-C), 146.9 (*p*-C), 134.2 (*o*-C), 119.5 (*m*-C), 67.8 (OCH_2), 35.0 (*m*- $\text{C}(\text{CH}_3)_3$), 32.3 (*m*- $\text{C}(\text{CH}_3)_3$), 25.2 (CH_2).

Reaction between **1 and Excess THF** (*vide infra* Figure 5). ^1H NMR: 8.08 (s, *o*-H), 7.21 (s, *p*-H), 3.52 (m, OCH_2), 1.46 (m, *m*- $\text{C}(\text{CH}_3)_3$ and CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR: 183.6 (*i*-C), 144.8 (*p*-C), 136.9 (*o*-C), 117.3 (*m*-C), 67.8 (OCH_2), 34.8 (*m*- $\text{C}(\text{CH}_3)_3$), 32.5 (*m*- $\text{C}(\text{CH}_3)_3$), 25.8 (CH_2). THF in C_6D_6 for comparison: ^1H NMR: 3.55 (m, OCH_2), 1.42 (m, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR: 67.7 (OCH_2), 25.8 (CH_2).

$(\text{LiC}_6\text{H}_4\text{-4-}t\text{-Bu})_n$ (2). A solution of $\text{Li}(t\text{-Bu})$ (20.8 mmol) in benzene (15 mL) was added dropwise to a solution of 4-*t*- $\text{BuC}_6\text{H}_4\text{Br}$ (2.22 g, 10.4 mmol) in benzene at room temperature. The solution gradually became warm, and a white, very fine precipitate began to form after *ca.* 5 min. Stirring was discontinued and the slurry was left standing at room temperature for *ca.* 20 h. This solution was then cooled in a 6 °C refrigerator for 5 days. Removal of the turbid, colorless supernatant liquid gave 0.65 g of microcrystalline **2**, which can be recrystallized from refluxing toluene to afford the product as very small colorless needles which were dried under reduced pressure. Yield: 44.6%. Mp: turns red at 170 °C; melts and turns dark red at 205–6 °C (dec). ^1H NMR (C_6D_6 , 23 °C): 7.86 (d, *o*-H, 2H), $^3J_{\text{HH}} = 6.9$ Hz, 7.27 (d, *m*-H, 2H), 1.25 (s, *p*- $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 85 °C): 150.6 (*p*-C), 140.6 (*o*-C), 125.8 (*m*-C), 34.4 (*p*- $\text{C}(\text{CH}_3)_3$), 31.4 (*p*- $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_7D_8 , 110 °C): 165.8 (*i*-C), 150.8 (*p*-C), 140.6 (*o*-C), 125.9 (*m*-C), 34.7 (*p*- $\text{C}(\text{CH}_3)_3$), 31.6 (*p*- $\text{C}(\text{CH}_3)_3$). ^7Li NMR (C_6D_6 , 23 °C, referenced to external LiCl in D_2O): 2.7 (s). Anal. Calcd for $\text{C}_{11.17}\text{H}_{13.34}\text{Li}$ ($1/2$, $2^{1/6}$ PhMe): C, 86.80; H, 8.70. Found: C, 86.31, H, 8.52. The compound **2** crystallizes as a solvate from both toluene and benzene. The ratio of $\text{LiC}_6\text{H}_4\text{-4-}t\text{-Bu}$ to C_6H_6 or PhMe is 6:1 by ^1H NMR. The solvent may be removed under reduced pressure.

$(\text{LiC}_6\text{H}_4\text{-4-}n\text{-Bu})_n$ (3). $\text{Li}(t\text{-Bu})$ solution (1.5 mL; 12.4 mL, 18.6 mmol) in *n*-pentane was added dropwise to a solution of 1.98 g (9.3 mmol) of 4-*n*- $\text{BuC}_6\text{H}_4\text{Br}$ in pentane at 0 °C. The slightly cloudy, pale yellow reaction mixture was slowly warmed to room temperature (*ca.* 2 h) and stirred for 3 days. The finely divided, off-white solid was collected on a glass frit, washed with *n*-pentane (30 mL), and was dried under reduced pressure. Yield: 1.63 g. The NMR spectra of this solid,

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which is sparingly soluble in hot C_6D_6 and is a mixture of **3** and *ca.* 20% LiBr on the basis of elemental analysis, are as follows. 1H NMR (C_6D_6 , 80 °C): 7.76 (d, *o*-H, 2H), $^3J_{HH} = 7.5$ Hz, 7.10 (d, *m*-H, 2H), 2.50 (t, α -CH₂, 2H), $^3J_{HH} = 7.5$ Hz, 1.57 (tt, β -CH₂, 2H), $^3J_{HH} = 7.5$ Hz, 1.30 (tq, γ -CH₂, 2H), 0.87 (t, CH₃, 3H), $^3J_{HH} = 7.5$ Hz. $^{13}C\{^1H\}$ NMR (C_6D_6 , 85 °C): 166.2 (*i*-C), 142.2 (*p*-C), 140.6 (*o*-C), 129.2 (*m*-C), 36.0 (α -C), 33.8 (β -C), 22.7 (γ -C), 13.9 (CH₃). 7Li NMR (C_6D_6 , 80 °C, referenced to external LiCl in D_2O): 2.2 (s). Attempts to extract pure **3** from this solid by using refluxing toluene (80 mL) led to a clear, red solution, from which 0.29 g of a pale, off-white, microcrystalline solid precipitated after cooling to room temperature. This solid, which appeared to be less soluble in hot C_6D_6 than the crude product, was identified as **3** by its conversion to $Me_3SiC_6H_4-4-n-Bu$ in 77% yield by the reaction with excess Me_3SiCl (1.0 mL) in 20 mL of *n*-pentane for 3 days at room temperature. Elemental analysis shows the presence of LiBr even after recrystallization.

[LiC₆H₄-4-SiMe₂-*t*-Bu]_n (4). Li(*t*-Bu) solution (1.5 M; 9.5 mL, 14.2 mmol) in pentane was added dropwise to a solution of 1.93 (7.1 mmol) $BrC_6H_4-4-SiMe_2-t-Bu$ in *ca.* 100 mL pentane at room temperature. After *ca.* 30 min, the reaction mixture became pale yellow and a fine white precipitate began to form. The reaction vessel was then cooled with a water bath. Stirring was discontinued after 4 h to allow the fine, voluminous precipitate (a mixture of **4** and LiBr) to settle. Because after 4 days the precipitate still occupied two-thirds of the reaction mixture, it was collected on a glass frit and dried under reduced pressure (crude yield, 0.97 g). Extraction with hot toluene (40 mL, 90 °C, 5 min), followed by decanting the slightly cloudy supernatant liquid and subsequent cooling to *ca.* -20 °C for 1 week, resulted in the isolation of 0.23 g of **4** (contaminated with LiBr) as a colorless microcrystalline solid (tiny needles), which was washed twice with *n*-pentane (2 × 20 mL) and dried under reduced pressure. Yield: 16.3%. 1H NMR(C_6D_6 , 22 °C): 7.76 (d, *o*-H, 2H), $^3J_{HH} = 6.9$ Hz, 7.44 (d, *m*-H, 2H), 0.93 (s, C(CH₃)₃, 9H), 0.25 (s, Si(CH₃)₂, 6H). $^{13}C\{^1H\}$ NMR(C_6D_6 , 22 °C): 169.8 (*i*-C), 139.5 (*o*-C), 136.5 (*p*-C), 134.7 (*m*-C), 26.8 (C(CH₃)₃), 17.2 (C(CH₃)₃), -6.1 (Si-CH₃). 7Li NMR(C_6D_6 , 22 °C): 2.4 (s). Mp: turns pink at 170 °C; gradually darkens until it melts and turns dark red at 205–7 °C.

X-ray Crystallography. Crystals suitable for X-ray crystallographic studies were grown from benzene (**1a**) or toluene (**1b**) solutions, and separate data sets were collected on each. Both crystal structures displayed disorder in four of the six crystallographically independent *t*-Bu groups (see Supporting Information). The crystals grown from benzene (i.e., **1a**) gave a superior data set and these data were used to calculate the structural parameters. Crystal data at 130 K are as follows. **1a:** $C_{84}H_{126}Li_6$, $M = 1177.49$, triclinic, space group $P\bar{1}$, $a = 13.516(2)$ Å, $b = 15.124(3)$ Å, $c = 20.958(3)$ Å, $\alpha = 84.084(13)^\circ$, $\beta = 86.249(11)^\circ$, $\gamma = 68.675(13)^\circ$, $V = 3967.7(11)$ Å³, $Z = 2$, $D_c = 0.986$ g cm⁻³, λ (Cu K α) = 1.54178 Å, $F(000) = 1296$, $\mu = 0.387$ mm⁻¹, 7983 reflections with $I > 2\sigma(I)$, $R_1 = 0.085$ and $wR_2 = 0.202$. **1b:** $C_{84}H_{126}Li_6$, $M = 1177.48$, triclinic, space group $P\bar{1}$, $a = 12.954(3)$ Å, $b = 13.487(3)$ Å, $c = 13.505(4)$ Å, $\alpha = 104.18(2)^\circ$, $\beta = 104.51(2)^\circ$, $\gamma = 111.19(2)^\circ$, $V = 1977.0(9)$ Å³, $Z = 1$, $D_c = 0.989$ g cm⁻³, λ (Cu K α) = 1.54178 Å, $F(000) = 648$, $\mu = 0.388$ mm⁻¹, 3938 reflections with $I > 2\sigma(I)$.

The structures were solved⁹ by using direct methods. Absorption corrections (XABS2) were applied to all data.¹⁰ Refinement was by full matrix least-squares methods based on F^2 with anisotropic thermal parameters for non-disordered non-hydrogen atoms. The occupancies of each disordered methyl carbon site are provided in the Supporting Information.

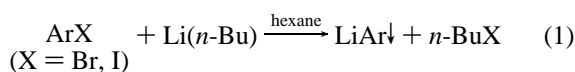
Results and Discussion

Synthesis. Initial experiments to test the Schlosser method¹¹ (illustrated by the generalized equation (1)) for the synthesis of compounds **1–4** showed that metal halogen exchange did indeed take place.

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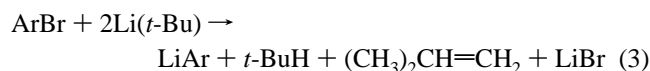
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For example, in the case of $[LiC_6H_4-4-t-Bu]_n$, NMR data revealed the slow formation of the lithium aryl which initially remains in solution. After a *ca.* 50% conversion, however, a white microcrystalline precipitate began to form and additional *n*-Bu signals appeared in the 1H NMR spectrum. These were assigned to 4-*t*-BuC₆H₄-*n*-Bu, which is the product of the competing reaction between LiAr and *n*-BuBr (eq 2).



This coupling reaction is apparently suppressed in the case of simple lithium aryl species such as LiPh or LiC₆H₄-4-Me by their insolubility in nondonor hydrocarbons. Thus, they are removed from the equilibrium by precipitation, which tends to drive the reaction in eq 1 to completion. For sterically hindered *ortho*-substituted aryls (i.e., compounds **A**, **B**, or **C**) this reaction also appears to be suppressed, but in this case it is probably for steric reasons. To minimize this coupling reaction the *meta*- and *para*-substituted aryl halides were lithiated by 2 equiv of the more reactive Li(*t*-Bu) according to the method of Seebach¹² (eq 3).



In this method the reaction between LiAr and *t*-BuBr is greatly diminished by the competing reaction between Li(*t*-Bu) and *t*-BuBr to afford LiBr, *t*-BuH, and $Me_2CH=CH_2$. Monitoring these reaction mixtures by NMR spectroscopy showed clearly the formation of the respective lithium aryls. In the case of the more soluble species $(LiC_6H_3-3,5-t-Bu)_6$ (**1**), the very fine (almost colloidal) LiBr precipitate was allowed to settle for several days, after which time the supernatant liquid was decanted, concentrated under reduced pressure, and cooled to *ca.* 6 °C for 1 week to afford the crystalline product in low yields (*ca.* ~20%). The compound $[LiC_6H_4-4-t-Bu]_n$ (**2**) crystallizes directly from the reaction mixture in the form of small colorless spherical aggregates (up to 1 mm diameter) which contain some benzene. Recrystallization from hot benzene or toluene affords small colorless needles of **2** which are solvates of the formula $LiC_6H_4-4-t-Bu \cdot 1/6 C_6H_6$ or $LiC_6H_4-4-t-Bu \cdot 1/6 PhMe$, as determined by 1H NMR. The molecules of the solvent may be evaporated under reduced pressure. The observation of the ratio of one solvent molecule per 6 equiv of lithium aryl in the case of both benzene and toluene supports the formulation of **2** as a hexamer.

The syntheses of $(LiC_6H_4-n-Bu)_n$ (**3**) and $(LiC_6H_4-4-SiMe_2-t-Bu)_n$ (**4**) are best conducted in *n*-pentane. The off-white solid crude products—a mixture of either **3** or **4** and LiBr¹³—were collected on a sintered glass frit, washed once with *n*-pentane, and dried under reduced pressure. Dissolving **3** in refluxing toluene gives a clear, red solution. Interestingly, the LiBr coproduct appears to be partly soluble under these conditions as well, and further recrystallization of **3** from toluene failed to remove all the LiBr. This suggests that it could be associated with the ArLi framework. However, it is notable that, at present, organolithium–lithium halide complexes have only been isolated as donor stabilized species as in $(LiPh \cdot Et_2O)_3 \cdot LiBr$,⁷ {Li-

(12) Seebach, D.; Neumann, H. *Chem. Ber.* **1974**, *107*, 847.

(13) Analyses of crude samples of compounds **3** and **4** showed that they were contaminated with *ca.* 20–30% LiBr. The carbon and hydrogen analyses are consistent with the remainder of the sample being the lithium aryl. Recrystallization reduced, but did not eliminate, the amount of included LiBr.

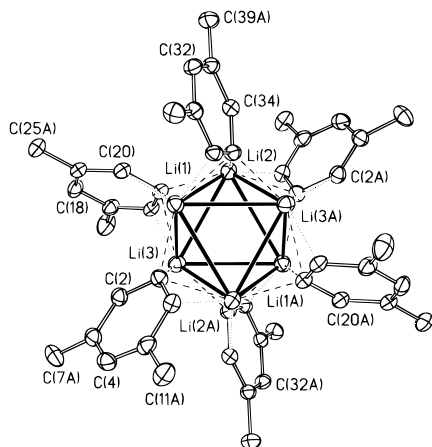


Figure 2. Thermal ellipsoid plot (30%) of one of the two independent molecules of **1**. Methyl groups and hydrogen atoms are not shown for clarity.

(*c*-CH)(CH₂)₂}₂•(LiBr)₂•Et₂O)₄,¹⁴ or the intramolecularly coordinated LiC₆H₃{CH₂N(Me)CH₂CH₂NMe₂}₂•2,6•LiBr.¹⁵ Cooling to room temperature affords feathery microcrystals, which with excess Me₃SiCl in pentane give 4-*n*-BuC₆H₄SiMe₃ in 77% yield. The aryllithium compound **4**, however, can be extracted from this mixture with hot toluene to give, after filtration and crystallization at -20 °C, dumbbell-shaped microcrystalline aggregates. So far, only crystals of **1** have proven suitable for X-ray crystallography. However, the availability of these enabled the first structural characterization of a simple, base-free, sterically unencumbered σ -bonded aryllithium compound.

Structure. (LiC₆H₃-3,5-*t*-Bu₂)₆ crystallizes from benzene in the triclinic space group *P*1̄ with two crystallographically independent, trimeric half-molecules in the asymmetric unit. These half-molecules are chemically equivalent, but one (i.e. incorporating Li(4), etc.), displays a slightly more irregular geometry than the other. There are no close contacts between the resultant hexamers, and the shortest intermolecular Li-C distance is 5.269 Å. Each hexameric molecule (Figure 2) involves a trigonal, antiprismatic array of lithiums in which there are six short (range 2.491(9)–2.545(9) Å, avg 2.52(2) Å) and six long (range 3.050(8)–3.270(9), avg 3.14(7) Å) Li-Li distances. The six aryl substituents triply bridge six of the eight triangular Li₃ faces and are bound principally through their *ipso*-carbon atoms. Two of the equilateral and opposite faces which involve the six longest Li-Li edges remain uncapped. The aryl groups do not bridge the Li₃ faces symmetrically since there is one short (range 2.119(7)–2.151(7) Å, avg 2.14(1) Å) and two longer (range 2.195(7)–2.247(7) Å, avg 2.22(1) Å) sets of Li-C(*ipso*) distances. Thus, each Li⁺ ion has a stronger interaction with a specific *ipso*-carbon, i.e. Li(1) with C(1), Li(2) with C(15), Li(3a) with C(29), etc. Furthermore, the short Li-C interactions have a greater σ -character since they are more closely aligned to the aryl ring plane, as evidenced by the relatively low angles (16.9–24.2°) between the Li-C and C(*ipso*)-C(*para*) lines (Figure 3). The remaining two long Li-C bonds at each lithium have more π -like character with angles between the Li-C and C(*ipso*)-C(*para*) vectors in the range 52.6–77.4°. This bonding configuration, which is very similar in the case of each lithium, also allows Li-C(*ortho*) interactions that are in the

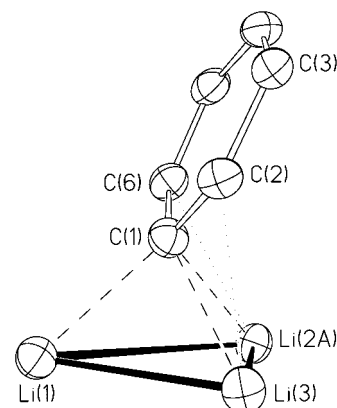


Figure 3. View of the aryl group interaction with one of the capped Li₃ triangles in **1**. No ring substituent atoms are shown.

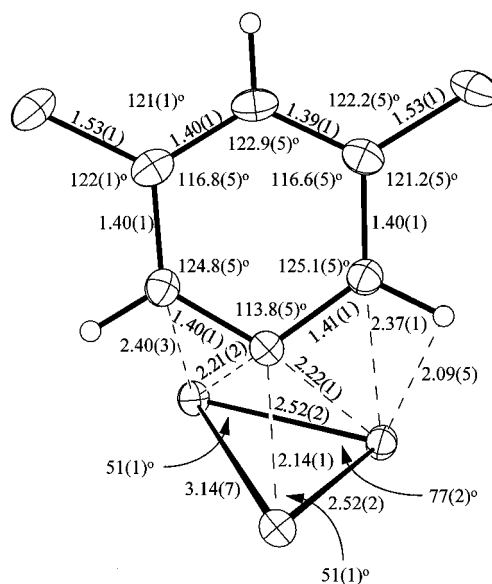


Figure 4. Schematic drawing summarizing the important average interatomic distances (Å) and angles in **1**.

range 2.36–2.47 Å. These weaker Li-C(*ortho*) interactions are also facilitated by the alignment of the phenyl ring above each Li₃ face. Similarly, relatively close Li-H contacts (in the range 2.06–2.52 Å) involving *ortho*-hydrogens of the aryl group may be calculated. The aromatic rings display the usual structural deviations associated with substitution of a hydrogen with an electropositive metal. The C-C-C angle at the *ipso*-carbon atoms, which formally carry the negative charge, is narrowed to 113.9° (avg) and this is accompanied by a slight lengthening of the C(*ipso*)-C(*ortho*) distances to 1.404 Å (avg). Important structural parameters for **1** are summarized in Figure 4.

The structure of **1** may be compared to those of the alkyl hexamers {Li(*c*-C₆H₁₁)₆}•2C₆H₆,¹⁶ {LiCH₂(*c*-CHCMe₂CMe₂)₆,¹⁷ {LiCH₂SiMe₃}₆,¹⁸ {Li(*i*-Pr)}₆,¹⁹ or {Li(*n*-Bu)}₆.²⁰ These compounds also possess distorted octahedral or trigonal prismatic structures with uncapped transoid Li₃ faces, except in the case of {Li(*c*-C₆H₁₁)₆}•2C₆H₆, where there are weak interactions with benzene. The six long Li-Li interactions in these structures

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(15) Wehman-Ooyevaar, I. C. M.; Kapteijn, G. M.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **1993**, *452*, C1-C-3.

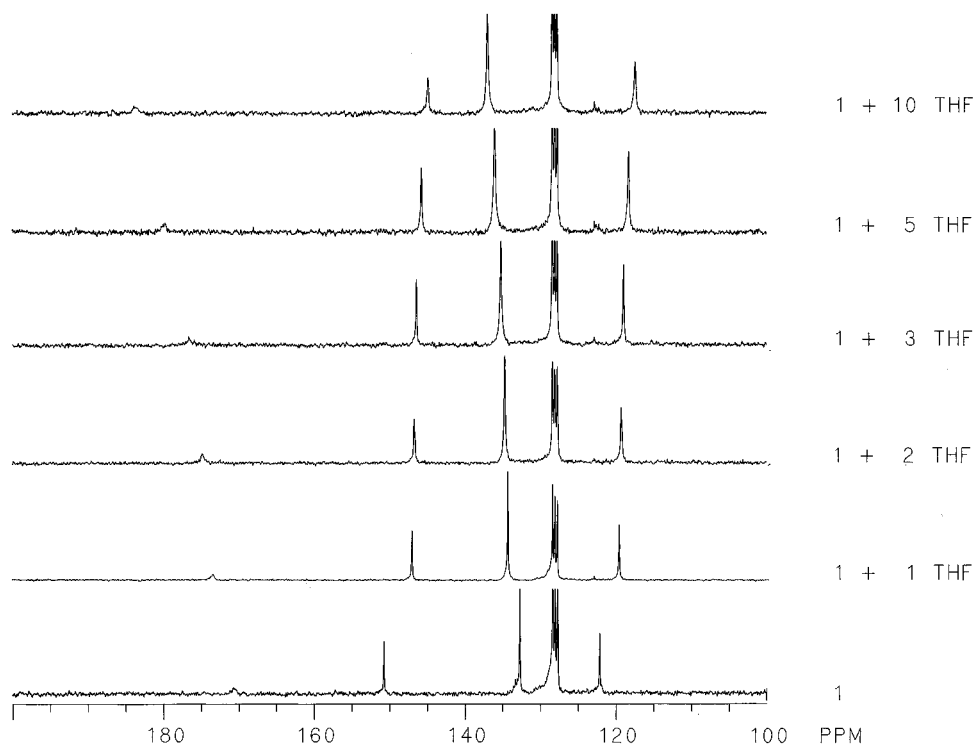


Figure 5. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** and **1** + 1, 2, 3, 5, and 10 equiv of THF in C_6D_6 at room temperature, which illustrate the conversion of $(\text{THF}\cdot\text{LiC}_6\text{H}_3\text{-3,5-}i\text{-Bu})_4$ (bottom) to $\{(\text{THF})_2\text{LiC}_6\text{H}_3\text{-3,5-}i\text{-Bu}\}_2$ (top).

are also associated with these uncapped Li_3 faces. The shorter and longer Li–Li distances in **1** may be compared with those observed in the hexameric alkyls. For instance, the short and long Li–Li interactions in $\{\text{Li}(i\text{-Pr})\}_6$ are in the ranges 2.388(3)–2.404(3) and 2.926(3)–3.014(3) Å, respectively, which are marginally (*ca.* 0.1 Å) shorter than those observed in **1**. The Li–C distance in **1** (avg 2.14(1) Å) is among the shortest observed in any associated base-free organolithium structure¹ and may be compared with the range of *ca.* 2.18–2.20 Å observed for the shorter Li–C bonds in the hexameric lithium alkyls mentioned above.^{16–20} The longer group of Li–C distances in **1** (avg 2.22(1) Å) is also shorter than those observed in the hexameric alkyls by a similar amount.

In essence, the structural parameters of **1** show that the Li–C bonding in **1** is significantly stronger than those in the corresponding alkyls and makes for a tighter aggregate overall. This is to be expected in view of the lower coordination number (i.e. five, cf. six in the alkyls) of the lithium bound *ipso*-carbon. In addition, the approximate sp^2 hybridization of the carbon bonding orbital, together with the presence of π -electron density, further enhance the lithium–carbon interactions.

NMR Studies. ^{13}C NMR spectroscopy of the lithium aryls **1–4** shows that they possess the usual strong downfield^{5b} shift in their *ipso*-carbon signals. The high temperatures of the measurements—due to the limited solubilities—result in a narrow *ipso*-carbon signal, suggesting fast exchange of the Li^+ ions and thereby precluding the determination of Li–C coupling constants. Their *ipso*-carbon chemical shifts are **1**, 170.6 ppm (C_6D_6 , 23 °C); **2**, 165.8 ppm (C_7D_8 , 110 °C); **3**, 166.2 ppm (C_6D_6 , 85 °C); and **4**, 169.8 ppm (C_6D_6 , 22 °C), which are relatively close to those of the solvates $(\text{Et}_2\text{O}\cdot\text{LiC}_6\text{H}_4\text{-4-Me})_4$ ^{6f} ($\delta = 170.2$ (C(*ipso*))) and $(\text{Et}_2\text{O}\cdot\text{LiPh})_4$ ($\delta = 174.2$ (C(*ipso*))) that also have tetrameric structures in ether solution. In the case of **3** and **4**, it could be argued that if lithium halide were included as part of their structures, the chemical shifts could be affected. However, we have compared the ^{13}C NMR spectra of $(\text{LiPh}\cdot\text{Et}_2\text{O})_4$ and $(\text{LiPh}\cdot\text{Et}_2\text{O})_3\cdot\text{LiBr}$, whose structures were

already established by X-ray crystallography.⁷ The ^{13}C NMR data for these compounds in ether solution (with *ca.* 10% C_6D_6 reference) show that there is only a small (*ca.* 2 ppm) difference in the shifts of *ipso*-carbons. Attempts to record the spectra of $(\text{LiPh}\cdot\text{Et}_2\text{O})_3\cdot\text{LiBr}$ in pure C_6D_6 led to the precipitation of LiBr and ^{13}C NMR resonances identical to those of $(\text{LiPh}\cdot\text{Et}_2\text{O})_4$. It is therefore concluded that the inclusion of small amounts of lithium halide in **3** and **4** seems to have only a minor influence of their *ipso*-carbon chemical shifts. The addition of 1 equiv of Et_2O or THF per lithium to C_6D_6 solutions of **1** led to only a slight change of the C(*ipso*) chemical shift to 171.1 or 173.4 ppm, respectively. Furthermore, these additions resulted in a dramatic increase in the solubility of **1** in benzene. Additional evidence of Et_2O or THF complexation to the Li^+ ions in **1** was provided by shifts in the δ values of the ether or THF protons and carbons. It may be tentatively concluded that, when **1** is treated with 1 equiv of Et_2O or THF per lithium, it forms 1:1 complexes which are tetrameric aggregates with structures very similar to those established for $(\text{Et}_2\text{O}\cdot\text{LiPh})_4$ and $(\text{Et}_2\text{O}\cdot\text{LiC}_6\text{H}_4\text{-4-Me})_4$ in ether.⁶

It has already been shown by a number of groups that *ipso*-carbon chemical shifts of the dimeric or monomeric solvated lithium aryls are significantly further downfield than the corresponding tetramers and are in the range of 180–200 ppm.⁶ Presumably, the greater downfield shift in these dimers or monomers is due to the lower coordination number (and lower shielding) of the C(*ipso*) carbon, which has a coordination number of four in the dimer and three in the monomer. The monomers and dimers were invariably obtained by the addition of a sufficient quantity of a Li^+ complexing donor molecule to break down the aggregation. In a similar manner, the addition of excess THF to **1** in C_6D_6 results in a downfield shift of *ipso*-C resonance to 183.6 ppm (Figure 5), which is consistent with the formation of the dimer $\{(\text{THF})_2\cdot\text{LiC}_6\text{H}_3\text{-3,5-}i\text{-Bu}\}_2$ (cf. 188.2 ppm for C(*ipso*) of LiPh in THF) under similar conditions.^{6c}

The C(*ipso*) chemical shifts of $(\text{LiTrip})_4$ ² ($\delta = 184.0$ (C(*ipso*))) or $(\text{LiC}_6\text{H}_3\text{-2,6-Dipp})_3$ ³ ($\delta = 186.0$ (C(*ipso*))) in

which Li^+ is both η^1 - σ -bonded and η^6 - π -bonded to different phenyl rings (structures **A** and **C**) also imply that the effective coordination number of the *C*(*ipso*) is lowered (i.e. to three) in these compounds. In contrast, the chemical shift for **1** is closer to that of $(\text{LiC}_6\text{H}_3\text{-2,6-Mes}_2)_2$ structure **B** ($\delta = 173.5$ (*C*(*ipso*))). In this case, although the *ipso*-carbons are four-coordinate, it appears reasonable to believe that the chemical shift so produced would be similar to that in **1**, where the five-coordinate *C*(*ipso*) has a weaker interaction with two Li^+ ions.

Conclusions

The first structural determination of a base-free, σ -bonded lithium aryl, which is not sterically encumbered by *ortho*-substituents, shows that it is hexameric in the crystalline phase. Moreover, the primary interaction between the lithiums and the aryl rings involves the *ipso*-carbon atom. There are also secondary interactions involving *ortho*-carbons, but there are no η^6 -aryl ring-Li linkages similar to those seen in the structures of $(\text{LiTrip})_4$ (**A**) or $(\text{LiC}_6\text{H}_3\text{-2,6-Dipp}_2)_2$ (**C**). The structure is thus quite different from the other three structures (i.e., **A**, **B**, and **C**) of unsolvated lithium aryls known at present. In essence, it is more representative of what the structure of a simple uncomplexed lithium aryl would resemble in the solid. Solution ^{13}C NMR for **1-4** strongly support a similarly associated structure in solution in the absence of Lewis bases. The addition of 1 equiv of Et_2O or THF per lithium to C_6D_6 solutions of **1** result in the formation of complexes, which on the basis of ^{13}C NMR data probably have the tetrameric formulae $(\text{Et}_2\text{O}\cdot\text{LiC}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2)_4$ and $(\text{THF}\cdot\text{LiC}_6\text{H}_3\text{-3,5-Bu}_2)_4$ with structures similar to that of $(\text{Et}_2\text{O}\cdot\text{LiPh})_4$.

The hexameric structure of **1** underlines the fact that the aggregation number six (rather than the more widely assumed four) is the most preferred one for unsolvated lithium alkyls or aryls. With sterically crowding groups and where there are intermolecular interactions, lower aggregation numbers (i.e. 2 or 4) are generally found. Thus, $[\text{Li}(t\text{-Bu})]_4$ ²⁰ and $\{\text{LiC}(\text{SiMe}_3)_3\}_2$ ²¹ are tetrameric and dimeric for steric reasons, and relatively close intermolecular interactions are in part responsible

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for the classic tetrameric structures $(\text{LiMe})_4$ ²² or $(\text{LiEt})_4$ ²³ which represent an intermediate stage between a molecular and a polymeric ionic structure. However, with groups that are large enough to prevent intermolecular interactions but not large enough to cause significant crowding (e.g. *i*-Pr, *c*- C_6H_{11} , CH_2 (*c*- $\text{CHCMe}_2\text{CMe}_2$), *n*-Bu, CH_2SiMe_3 , $\text{C}_6\text{H}_3\text{-3,5-}t\text{-Bu}_2$), hexameric structures of the lithium derivatives are observed, and this aggregation number is currently the most commonly seen in the solid state for unsolvated lithium alkyls or aryls.²⁴

Does LiPh have a hexameric structure like **1** in the solid? The similarities between the spectroscopy of **1**, its ether or THF adduct, and the corresponding uncomplexed and complexed LiPh derivatives suggest that the answer is probably yes. The observation of one-sixth solvent molecule per aryllithium unit in the benzene and toluene solvates of **2** lends further credence to this view. However, it has been proposed^{df} that the insolubility of LiPh in hydrocarbons is due to intermolecular interactions (cf. $(\text{LiMe})_4$ structure) between $(\text{LiPh})_2$ dimers that stack continuously to give polymers with four-coordinate lithium. Although the results in this paper do not preclude this possibility, it is probable that the solubility of a putative $(\text{LiPh})_6$ hexamer in such solvents would also be extremely low.

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Supporting Information Available: Full tables of the data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters together with notes on structure solution and refinement (22 pages). See any current masthead page for ordering and Internet access instructions.

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(24) Organolithium compounds with aggregation numbers higher than six (e.g. $\text{Li}(n\text{-Pr})_8$ or $\text{Li}(n\text{-Pr})_6$) have been detected in solution at low temperatures. Nonetheless, at room temperature the hexameric structure predominates: Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 3345.