Isolation and Structural Characterization of Unsolvated Lithium Aryls

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Abstract: The synthesis and characterization of three examples of unsolvated lithium aryls are described. The compounds $\{\mathrm{Li(Trip)}\}_4$ (**1**, Trip = 2,4,6-*i*-$\mathrm{Pr_3C_6H_2}$), $\{\mathrm{Li(2,6\text{-}Mes_2C_6H_3)}\}_2$ (**2**, Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$), $\{\mathrm{Li}(n\text{-}\mathrm{Bu})\}_2(\mathrm{LiMes^*})_2$ (**3**), and $\{\mathrm{Li}(n\text{-}\mathrm{Bu})\}_2(\mathrm{LiMes^*})_2\cdot\mathrm{Mes^*Br}$ (**3**·Mes*Br, Mes* = 2,4,6-*t*-$\mathrm{Bu_3C_6H_2}$) were synthesized by a metal–halogen exchange reaction between *n*-butyllithium and the appropriate aryl bromide (**1** and **3**) or iodide (**2**). The X-ray crystal structures of **1** and **3** show that they are tetrametallic lithium species involving almost planar arrays of four lithium atoms. The bonding involves both σ- and π-interactions to the aryl ligands. In contrast, the structure of **2** is dimeric with the two aryl groups linked by two μ_2-bridging lithiums which are primarily σ-bonded to ipso carbons. Weaker interactions were also observed between the ortho mesityl substituents and the lithiums. The structure of **3**·Mes*Br shows that the halide starting material Mes*Br can be included in the isolated crystals. This is a consequence of the fact that the metal–halogen exchange reaction used in their synthesis is sluggish. The main reasons for this probably are the use of hydrocarbon rather than ether solvent and the large size of the aryl ligands. The compounds were characterized by ^{1}H, ^{13}C, and ^{7}Li NMR spectroscopy and X-ray crystallography and represent the first examples of structurally characterized simple, nonsolvated, σ-bonded lithium aryls. Crystal data with Mo Kα (λ = 0.71069 Å) at 130 K: **1**, $a = b = 13.098(2)$ Å, $c = 16.791(8)$ Å, $V = 2881(2)$ Å^3, $Z = 2$, space group $I\bar{4}$, 597 ($I > 2\sigma(I)$) data, $R = 0.089$; **2**, $a = 30.190(7)$ Å, $b = 13.423(2)$ Å, $c = 19.048(4)$ Å, $V = 7719(3)$ Å^3, $Z = 8$ (two independent molecules), space group *Pnna*, 3419 ($I > 2\sigma(I)$) data, $R = 0.097$; **3**, $a = 22.721(11)$ Å, $b = 10.072(5)$ Å, $c = 19.327(8)$ Å, $V = 4423(3)$ Å^3, $Z = 4$, space group $Pna2_1$, 1811 ($I > 2.5\sigma(I)$) data, $R = 0.082$; **3**·Mes*Br, $a = 11.385(2)$ Å, $b = 15.261(3)$ Å, $c = 17.458(5)$ Å, $\beta = 91.16(2)$°, $V = 3032.4(12)$ Å^3, $Z = 2$, space group C_2/m, 1821 ($I > 3\sigma(I)$) data, $R = 0.104$.

Introduction

During the last four decades the use of organolithium compounds has increased to the extent that they now play a central role in chemical synthesis.[1,2] In certain respects, they have greater flexibility than Grignard reagents since they display higher reactivity and, in many instances, they do not require the use of donor solvents in their preparation. The importance of organolithium reagents had led to considerable interest in their structures.[3] The structural data show that they display a strong tendency to associate and/or form complexes with donor molecules. In addition, the majority of structures in the crystal phase involve complexes with amine or ether molecules which coordinate to the lithium ion. Structural determinations of simple, uncomplexed organolithium compounds, in which there is a σ-interaction between the lithium centers and the organic moieties, are much less common and are mainly confined to alkyl species. The main objectives of the work described here were to isolate and characterize unsolvated lithium aryls with an Li–C σ-interaction and to compare their structures with those of lithium alkyls. In this paper, the synthesis and characterization of the compounds $(\mathrm{LiTrip})_4$ (**1**, Trip = 2,4,6-*i*-$\mathrm{Pr_3C_6H_2}$), $\{\mathrm{Li(2,6\text{-}Mes_2C_6H_3)}\}_2$ (**2**, Mes = 2,4,6-$\mathrm{Me_3C_6H_2}$), and the mixed lithium alkyl–aryl species $\{\mathrm{Li}(n\text{-}\mathrm{Bu})\}_2(\mathrm{LiMes^*})_2$ (**3**) and **3**·Mes*Br (Mes* = 2,4,6-*t*-$\mathrm{Bu_3C_6H_2}$) are now described. They represent the first structurally characterized examples of simple unsolvated lithium aryls.

Experimental Section

General Procedures. All experiments were performed under nitrogen atmosphere either by using modified Schlenk techniques or in a Vacuum Atmospheres HE 43-2 drybox. Solvents were freshly distilled from a sodium–potassium alloy and degassed twice prior to use. ^{13}C, ^{1}H, and ^{7}Li NMR spectra were recorded in $\mathrm{C_6D_6}$ or $\mathrm{C_7D_8}$ solutions by using a General Electric QE-300 spectrometer. The compounds 2,4,6-*i*-$\mathrm{Pr_3C_6H_2Br}$ (TripBr)[4], 2,6-$\mathrm{Mes_2C_6H_3I}$,[5] and 2,4,6-*t*-$\mathrm{Bu_3C_6H_2Br}$ (Mes*Br)[6] were synthesized by literature procedures. *n*-BuLi (1.6 M solution in hexanes) was purchased commercially and used as received.

Synthesis. (a) $\{\mathrm{Li(2,4,6\text{-}}i\text{-}\mathrm{Pr_3C_6H_2)}\}_4$ ($(\mathrm{LiTrip})_4$, 1). With rapid stirring, TripBr (5 g, 17.6 mmol), dissolved in *n*-hexane (50 mL), was treated with *n*-BuLi (16 mL of a 1.6 M solution in hexanes, 25.6 mmol, ca. 50% excess of maximize yield). The solution was warmed to ca. 50 °C for 24 h by which time it had become slightly cloudy. Concentration to ca. 50% of the original volume, filtration, and storage of the filtrate in a –20 °C freezer overnight afforded colorless crystals of **1**. Concentration of the mother liquor to ca. 10 mL and further cooling resulted in an additional crop of crystals: yield 3.34 g, 15.9 mmol, 90%; mp 180 °C dec (the crystals become black); ^{1}H NMR ($\mathrm{C_7D_8}$) 7.03 (s, *m*-H), 2.77 (sept, *p*-C*H*$\mathrm{Me_2}$, $^3J_{\mathrm{HH}} = 6.8$ Hz), 2.65 (sept, *o*-C*H*$\mathrm{Me_2}$, $^3J_{\mathrm{HH}} = 6.8$ Hz), 1.32 (d, *o*-CH*Me*$_2$), 1.21 (d, *p*-CH*Me*$_2$); ^{13}C{^{1}H} NMR ($\mathrm{C_7D_8}$, –20 °C) 184.0 (br, s, ipso-C), 161.3 (s, *o*-C), 145.3 (s, *p*-C), 117.07 (s, *m*-C), 40.2 (s, *o*-*CH*$\mathrm{Me_2}$), 34.43 (s, *p*-*CH*$\mathrm{Me_2}$), 24.83 (s, *p*-CH*Me*$_2$), 20.4 (s, *o*-CH*Me*$_2$); ^{7}Li NMR ($\mathrm{C_7D_8}$) –5.16 (s).

(b) $\{\mathrm{Li(2,6\text{-}Mes_2C_6H_3)}\}_2$ (2). With rapid stirring, 2,6-$\mathrm{Mes_2C_6H_3I}$ (4.4 g, 10 mmol) was dissolved in hexane (60 mL) and *n*-BuLi (6.25 mL of 1.6 M solution in hexanes) was added via syringe. The solution became cloudy upon stirring overnight. After filtration through a Celite padded medium porosity frit, the volume of the filtrate was reduced to incipient crystallization. Slight warming afforded a clear solution which upon cooling overnight in a –20 °C freezer afforded the product **2** as large

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Table I. Crystallographic Data for **1**, **2**, and **3** and **3**·Mes*Br[a]

compd	1	2	3	3·Mes*Br
formula	$C_{60}H_{92}Li_4$	$C_{48}H_{50}Li_2$	$C_{44}H_{72}Li_4$	$C_{62}H_{105}BrLi_4$
fw	841.1	640.76	628.8	958.17
crystal description	colorless cube	colorless parallelpiped	colorless block	colorless block
crystal size	0.15 × 0.15 × 0.21	0.15 × 0.19 × 0.43	0.5 × 0.5 × 0.3	0.35 × 0.43 × 0.54
a, Å	13.098(2)	30.190(7)	22.721(11)	11.385(2)
b, Å	13.098(2)	13.423(2)	10.072(5)	15.261(3)
c, Å	16.791(8)	19.048(4)	19.327(8)	17.458(5)
β, deg				91.16(2)
V, Å^3	2881(2)	7719(3)	4423(3)	3032.4(12)
Z	2	8 (two independent molecules)	4	2
space group	$I\bar{4}$	*Pnna*	$Pna2_1$	C_2/m
d(calc), (g/cm^3	0.97	1.103	0.944	0.958
linear abs coeff, cm^{-1}	0.53	0.61	0.51	7.07
2θ range, deg	0–46	0–55	0–50	0–55
no. of obsvd reflcns	597 ($I > 2\sigma(I)$)	3419 ($I > 2\sigma(I)$)	1811 ($I > 2.5\sigma(I)$)	1821 ($I > 3\sigma(I)$)
no. of variables	145	456	433	250
R, R_w	0.089, 0.101	0.097, 0.050	0.082, 0.085	0.104, 0.104

[a] The intensity data sets were collected at 130 K using a Siemens R3 m/V diffractometer with Mo Kα (λ = 0.71069 Å) radiation.

colorless crystals: yield 2.56 g, 80%; mp 164–166 °C (the crystals become yellow at ca. 140 °C); ^{1}H NMR (C_7D_8) 7.21 (t, *p*-H, $^3J_{HH}$ = 9.4 Hz), 6.86 (s, *m*′-H), 6.75 (d, *m*-H), 2.24 (s, *p*′-CH_3), 1.83 (s, *o*′-CH_3); $^{13}C\{^1H\}$ NMR (C_7D_8) 173.5 (s, br, ipso-C), 151.7 (s, *o*-C), 143.08 (ipso′-C), 137.2 (*p*′-C), 136.1 (*o*′-C) 129.9–121.5 (m, various *m* and *p* carbons) 21.3 (s, *o*′-Me), 20.7 (s, *p*-Me); ^{7}Li NMR (C_7D_8) 2.58 (s).

(c) {Li(*n*-Bu)}$_2$(LiMes*)$_2$ (3) and {Li(*n*-Bu)}$_2$(LiMes*)$_2$·Mes*Br (4). MEs*Br (3.25 g, 10 mmol) was dissolved in *n*-hexane (50 mL). With cooling in an ice bath and rapid stirring, *n*-BuLi (6.25 mL of a 1.6 M solution of *n*-hexanes) was added dropwise via a syringe. The cloudy solution was stirred for 30 h while being warmed to room temperature. The white precpitate was removed by filtration, and the volume of the solution was reduced to ca. 30 mL. Storage of this solution at –20 °C for ca. 10 h afforded colorless crystals of **3**: yield 0.44 g (0.7 mmol, 7%); mp dec >95 °C (the crystals become yellow). The mother liquor was kept in the –20 °C freezer for ca. 50 h during which time crystals of {Li(*n*-Bu)}$_2$(LiMes*)$_2$·Mes*Br were formed; yield 2.78 g (2.9 mmol, 29%); mp dec >95 °C (the crystals become yellow); ^{1}H NMR (C_7D_8) 7.49 (s, *m*-H (Mes*Br)), 7.47 (s, *m*-H), 1.60 (s, *o*-CH_3(Mes*Br)), 1.42 (s, *o*-CH_3), 1.37 (m, obscured by Mes* peaks, β,γ-H), 1.32 (s, *p*-CH_3), 1.26 (s, *p*-CH_3(Mes*Br)), 1.02 (m, δCH_3), –1.02 (m, α-H); ^{13}C NMR (C_7D_8) 173.5 (broad unresolved signal ipso-C), 163.8 (*o*-C), 149.1 (*o*-C(Mes*Br)), 148.7 (*p*-C), 147.3 (*p*-C(Mes*Br)), 124.0 (*m*-C(Mes*Br)), 122.4 (ipso-C(Mes*Br)), 118.1 (*m*-C), 38.8 (*o*-CMe_3), 38.6 (*o*-CMe_3(Mes*Br)), 35.1 (*p*-CMe_3(Mes*Br)) 34.9 (*p*-CMe_3), 33.7 (*o*-CH_3), 33.4 (β-C), 32.3 (*p*-CH_3(Mes*Br)), 31.9 (γ-C), 31.5 (*p*-CH_3), 31.2 (*o*-CH_3(Mes*Br)), 14.2 (δ-C), 12.2 (broad unresolved signal α-C); ^{7}Li NMR (C_7D_8) –1.22 (s).

X-ray Data Collection, the Solution and Refinement of the Structures. Crystals of **1**–**3** and **3**-Mes*Br were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. Suitable crystals were selected, attached to a glass fiber by silicon grease, and immediately placed in the low-temperature N_2 stream.[7] X-ray data were collected with a Siemens R3 m/V diffractometer equipped with a graphite monochromator and a locally modified LT apparatus. Calculations were carried out on a MicroVax 3200 computer using the SHELXTL-Plus program system.[8] Neutral atom scattering factors and the correction for anomalous dispersion were those supplied by SHELXTL Plus. Some details of the data collections and the refinements are provided in Table I. Further details are available in the supplementary material. All structures were solved by direct methods. The compounds were refined by full-matrix least-squares procedures. Hydrogen atoms were included by the use of a riding model with C–H distances of 0.96 Å and fixed isotropic thermal parameters with $U_{H^{iso}}$ = 0.08 (**1**), 0.06 (**2**), 0.06 (**3**), and 0.05(1) (**3**·Mes*Br) Å^2, respectively. The isopropyl groups in **1** show large thermal ellipsoids, indicating the structural flexibility of these groups; no disorder was apparent. In **3**, the *tert*-butyl groups of the Mes* unit and C(20) (i.e. α-C from *n*-Bu) were found to be disordered. They were refined by the use of split positions with 50% occupancy. In **3**·Mes*Br the Mes*Br molecule was disordered over 2 positions; these were refined in two positions both of which had 50% occupancy, and the refinement of this unit was not satisfactory which, in part, explains the high *R* value. Important bond distances and angles are given in Table II.

Results

Structural Descriptions. (a) (LiTrip)$_4$ (1). The molecular structure of **1**, which is illustrated in Figure 1, consists of tetramers which are generated (by a $\bar{4}$ symmetry axis) from an asymmetric unit containing a single LiTrip molecule. The lithium is η^1,σ-bonded to the C(1) of this aromatic ring and is η^6,π-bonded to another aromatic ring rotated 90° with respect to the first around the 4-fold symmetry axis. The Li–C(1) distance is 2.12(2) Å whereas the Li–C π-interactions are in the range of 2.28(2)–2.37(3) Å. The six aromatic ring carbons are coplanar within experimental error and there is an angle of 7.6° between the Li–C(1) and C(1)–C(4) vectors.

(b) {Li(2,6-Mes$_2$C$_6$H$_3$)}$_2$ (2). The basic structural motif of **2** consists of dimeric molecules. Two crystallographically independent, but chemically identical, dimers are generated (one by an inversion center, the other by a C_2 axis) from two monomeric moieties per asymmetric unit. One of these molecules is illustrated in Figure 2. The C(1), C(7), and C(11) phenyl rings interact with the lithiums through one carbon only (an η^1,π-interaction with Li–C distances in the range 2.16(1)–2.19(1) Å). The lithiums are thus μ_2 with respect to these phenyl rings. In addition, Li(1) and Li(2) have fairly close interactions (2.51(1)-2.56(1) Å) with ipso carbons (C(21), C(61), C(81), and C(91)) of the mesityl substituents.

(c) {Li(*n*-Bu)}$_2$(LiMes*)$_2$ (3). The molecules of **3** have no crystallographically imposed symmetry restrictions as illustrated in Figure 3. They are formed by the association of two Li(*n*-Bu) and two LiMes* units such that there exists an approximately planar array of four lithium centers bridged alternately by η^1,μ_2-*n*-Bu and η^1,η^6,μ_2-Mes* groups. The bonds between the lithiums and the *n*-Bu carbons C(19) and C(41) are in the range 2.03(3)-2.19(2) Å with similar Li–η^1-Mes* ring interactions of 2.05(2) and 2.07(2) Å. The aromatic rings possess η^6-interactions with Li(2) and Li(4) that are in the range 2.28(2)–2.45(2) Å. There are also close interactions between the ortho *t*-Bu groups of the Mes* moiety and Li(1) and Li(3) with Li···C distances in the range 2.55(2)–2.66(2) Å.

{Li(*n*-Bu)}$_2$(LiMes*)$_2$·Mes*Br (3·Mes*Br). The alkyl/aryl lithium molecules of **3**·Mes*Br possess a 2-fold axis of symmetry through the center of the molecule. The structure has an almost planar array of four lithium centers and displays very similar features to those of **3**. The bond distance between the lithium

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Table II. Important Bond Distances (Å) and Angles (deg) in **1**, **2**, **3**, and **3**·Mes*Br

1			
Li(1)–C(1)	2.12(2)	Li(1)–C(1)–Li(1a)	120.4(10)
Li(1)–C(1a)	2.34(2)	C(1)–Li(1)–C(1a)	149.0(10)
Li(1)–C(2a)	2.28(2)	C(1)–Li(1)–C(2a)	145.5(12)
Li(1)–C(3a)	2.28(3)	C(1)–Li(1)–C(3a)	137.0(12)
Li(1)–C(4a)	2.34(2)	C(1)–Li(1)–C(4a)	135.7(10)
Li(1)–C(5a)	2.37(2)	C(1)–Li(1)–C(5a)	140.6(12)
Li(1)–C(6a)	2.33(2)	C(1)–Li(1)–C(6a)	149.9(13)
2			
C(1)–Li(1)	2.17(1)	C(7)–Li(2)	2.20(1)
C(1)–Li(1a)	2.16(1)	C(7)–Li(2a)	2.20(1)
C(6)···Li(1a)	2.70(1)	C(8)···Li(2)	2.73(1)
C(21)···Li(1)	2.51(1)		
C(61)···Li(1a)	2.56(1)	Li(2)–C(11)	2.19(1)
Li(1)···Li(1a)	2.27(2)	Li(2)···Li(2a)	2.31(2)
		Li(2)···C(91)	2.56(1)
		Li(2)···C(12)	2.70(1)
		C(11)–Li(2a)	2.19(1)
Li(1a)–C(1)–Li(1)	63.2(5)	C(11)–Li(2)–C(7)	116.5(5)
C(1a)–Li(1)–C(1)	116.8(5)	C(11)–Li(2)–C(81)	145.0(5)
C(1a)–Li(1)–C(21)	146.1(5)	C(7)–Li(2)–C(81)	143.4(3)
C(1)–Li(1)–C(21)	64.4(3)	C(7)–C(8)–C(81)	119.4(5)
C(1a)–Li(1)–C(61a)	64.1(3)	C(11)–C(12)–C(91)	118.0(5)
C(21)–Li(1)–C(61a)	134.1(5)		
C(1a)–Li(1)–C(2)	143.1(5)		
3			
Li(1)–C(1)	2.05(2)	Li(3)–C(23)	2.07(2)
Li(1)···C(8)	2.55(2)	Li(3)···C(30)	2.60(2)
Li(1)···C(16)	2.66(2)	Li(3)···C(40)	2.65(2)
Li(1)···C(19)	2.19(2)	Li(3)–C(41)	2.09(2)
Li(2)–C(19)	2.03(3)	Li(4)–C(1)	2.28(2)
Li(2)–C(23)	2.32(2)	Li(4)–C(2)	2.29(2)
Li(2)–C(24)	2.30(2)	Li(4)–C(3)	2.35(2)
Li(2)–C(25)	2.36(2)	Li(4)–C(4)	2.45(2)
Li(2)–C(26)	2.37(2)	Li(4)–C(5)	2.41(2)
Li(2)–C(27)	2.34(2)	Li(4)–C(6)	2.30(2)
Li(2)–C(28)	2.35(2)	Li(4)–C(41)	2.06(2)
C(1)–Li(1)–C(19)	177.2(6)	C(23)–Li(3)–C(41)	174.1(10)
Li(1)–C(19)–Li(2)	90.0(8)	Li(3)–C(41)–Li(4)	89.4(8)
C(19)–Li(2)–C(23)	154.2(10)	C(41)–Li(4)–C(1)	152.6(9)
3·Mes*Br			
Li(1)–C(1)	2.07(2)	Li(2)–C(2a)	2.25(3)
Li(1)···C(9)	2.57(2)	Li(2)–C(3a)	2.35(3)
Li(1)–C(19)	2.17(2)	Li(2)–C(4a)	2.47(2)
Li(2)–C(19)	2.04(2)	Li(2)–C(5a)	2.46(3)
Li(2)–C(1a)	2.27(2)	Li(2)–C(6a)	2.41(3)
C(1)–Li(1)–C(19)	168.1(8)	C(19)–Li(2)–C(4a)	128.1(9)
C(9)–Li(1)–C(19)	95.5(8)	C(19)–Li(2)–C(5a)	138.6(12)
C(19)–Li(2)–C(1a)	156.2(10)	C(19)–Li(2)–C(6a)	152.0(15)
C(19)–Li(2)–C(2a)	145.2(15)	Li(1)–C(19)–Li(2)	90.3(8)
C(19)–Li(2)–C(3a)	130.0(13)		

atom and the ipso *n*-Bu carbon C(19) is 2.17(2) Å and the Li(1)–C(1) σ-interaction to the aromatic ring is 2.07(2) Å. The Li–η^6-aryl ring contacts are in the range 2.25(2)–2.49(2) Å with the shortest distance associated with the ipso carbon center. The ortho *t*-Bu interactions with the lithiums span the range 2.568–2.674 Å.

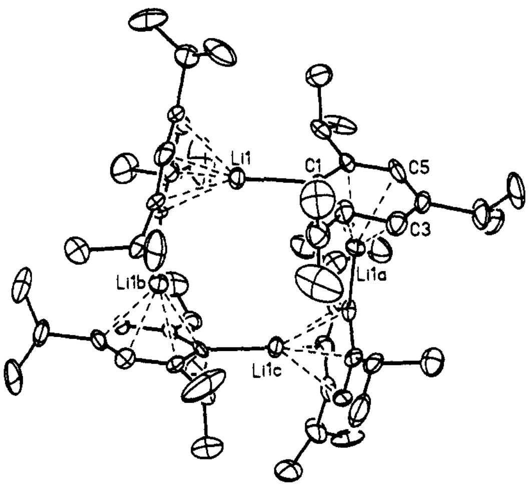

Figure 1. Computer-generated plot of **1** (thermal ellipsoids show 30% occupancy). The H atoms are omitted for clarity.

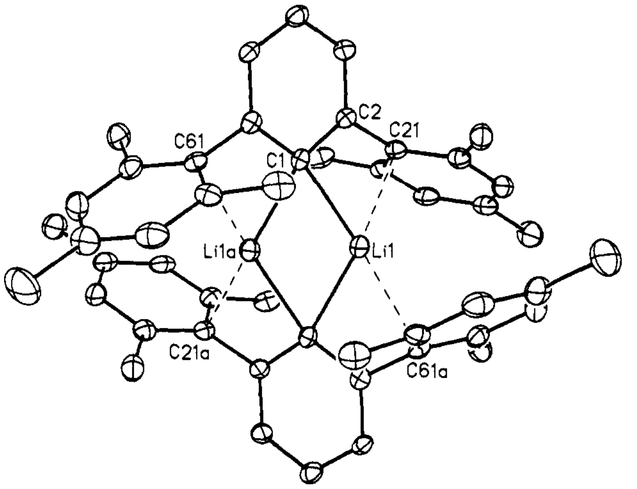

Figure 2. Computer-generated plot of one of the two independent molecules of **2** (thermal ellipsoids show 30% occupancy). The H atoms are omitted for clarity.

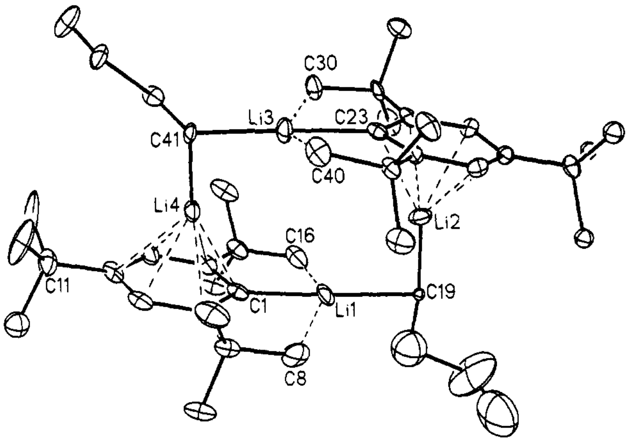

Figure 3. Computer-generated plot of **3** (thermal ellipsoids show 30% occupancy). The H atoms are omitted for clarity.

Discussion

Although the structures of several nonsolvated lithium alkyls (e.g. $(LiMe)_4$,[9] $(LiEt)_4$,[10] $\{Li(c\text{-}CH_2(Me)CH_2)\}_4$,[11] $\{Li(t\text{-}Bu)\}_4$,[12] $\{Li(c\text{-}C_6H_{11})\}_6$,[13] $(LiCH_2SiMe_3)_6$,[14] $\{Li(n\text{-}Bu)\}_6$,[12] and $\{LiCH(SiMe_3)_2\}_\infty$[15]) as well as one example of an unsolvated vinyllithium species, [α-(1,1,3,3-tetramethyl-2-indarylidene)benzyl]lithium), are now well-established,[16] the structure of a simple, nonsolvated, σ-bonded lithium aryl remains to be defined. The simplest lithium aryl, phenyllithium, has no appreciable solubility in nondonor

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solvents. It is readily soluble, however, in ether or THF and can be crystallized as the tetramer $\{Li(Et_2O)Ph\}_4$ from the former solvent.[17] The use of chelating ligands such as *N,N,N′,N′*-tetramethylenediamine (TMEDA) or *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) affords dimeric $\{Li(TMEDA)Ph\}_2$[18] or monomeric Li(PMDETA)Ph[19] complexes. Lower aggregation numbers can also be induced by increased crowding at the aryl group as observed in the dimers $\{Li(THF)_2Mes\}_2$[20] or $\{Li(Et_2O)Trip\}_2$[21] or the monomers $Li(Et_2O)_2(2,4,6\text{-}Ph_3C_6H_2)$[22,23] or $Li(Me_2NCH_2CH(Me)NMe_2)Mes^*$.[24] Threefold aggregation may be obtained by using intramolecular donor ligands as in $[Li\{2,6\text{-}(Me_2N)_2C_6H_3\}]_3$,[25] $[Li\{2,6\text{-}(t\text{-}BuO)_2C_6H_3\}]_3$,[26] or $[Li\{2\text{-}Me_2N(6\text{-}t\text{-}BuO)C_6H_3\}]_3$.[27] Clearly, all of these molecules involve extensive inter- or intramolecular solvation of the lithium by oxygen or nitrogen centered donor ligands. Currently, the only σ-bonded lithium aryl without ligand solvation at any lithium is the unique species $[\{Na(TMEDA)\}_3][LiPh_4]$[28] whose structure may be visualized as an Li^+ ion surrounded, in a distorted tetrahedral fashion, by four σ-bonded phenyl anions with Li–C distances in the range 2.23(2)–2.43(2) Å. Three sodium ions, each solvated by a TMEDA ligand, are associated with the anion through interactions with the ipso carbons of the phenyl groups. In addition, there are a number of structures of 1,1′-dilithioferrocenes in which some of the lithiums bridge the cyclopentadienide ligands and are not solvated by other donor ligands.[29]

There have also been a number of NMR studies of LiPh and related species in both solution[30–34] and solid phases.[35] Phenyllithium has been shown to be tetrameric in Et_2O solution[32] with a structure very similar to that reported in the crystal.[17] In dilute solution tetrameric and dimeric aggregates are apparently in equilibrium.[33] In THF, the structure of phenyllithium was reported to be dimeric[33,34] at both room temperature and –120 °C. In dilute (0.26 M) THF solution, however, there is a monomer–dimer equilibrium.[33] In the solid state, cross polarization/magic angle spinning (CP/MAS), ^{13}C NMR experiments have been performed to correlate the solution and X-ray data.[35] Excellent agreement was found for the complexes $\{Li(Et_2O)_2Ph\}_4$, $\{Li(TMEDA)Ph\}_2$, and Li(PMDETA)Ph, where there is a close structural correspondence between the compounds in the solution and solid phases. Uncomplexed LiPh was also studied in the solid phase and the data were interpreted on the basis of a tetrameric structure owing to the similarity of the ^{13}C NMR shifts to those of $\{Li(Et_2O)Ph\}_4$.[35] There has also been a proposal that the uncomplexed LiPh is polymeric in the solid state being composed of $(LiPh)_2$ rings that stack to give a structure with four-coordinate lithium atoms.[34]

The first of the three compounds to be examined in this work, $(LiTrip)_4$ (**1**), has a structure which has not been observed for any other aryllithium species. There is, however, some resemblance to the recently reported structure of the mixed lithium aryl/lithium phosphido species $(LiMes^*)_2\{LiP(H)Mes^*\}_2$[36] (vide infra). The structure of **1** involves an almost planar arrangement of four lithiums with only minor (<0.02 Å) deviation by opposite pairs of metals ($\bar{4}$ symmetry) above and below the least-squares plane. The ipso-carbons, however, show a more substantial deviations of *ca.* 0.17 Å on either side of this plane. The lithiums are σ-bonded to just one phenyl ring with an Li–C bond length of ca. 2.12 Å, which is in the range normally observed for low (2 or 3) coordinate lithium environment.[3,22] The average Li–C π-interaction, ca. 2.33 Å, is at the shorter end of the scale of values previously observed for related Li–C η^6,π-complexes.[36–38] In effect, the π-electron system of the aromatic ring plays a solvating role, while the *i*-Pr substituents provide solubility in hydrocarbon solvents. In the ^{13}C NMR spectrum the chemical shift of the ipso carbon, δ 184.0, is significantly different from that of LiPh in the solid or ether solutions. The shift observed is nearer to values for the $(LiPh)_2$ dimer and the LiMes monomer in THF. Thus, although **1** is a tetramer in the solid state and is presumably also a tetramer in hydrocarbon solvents, it displays ^{13}C NMR ipso-carbon δ values that are characteristic of a lower number of ipso-C–Li interactions. This is, of course, consistent with the X-ray data which indicate a single ipso-C–Li σ-bond in addition to a weaker ipso-C–Li π-interaction. The 4-fold aggregation in **1** may be easily disrupted by the addition of ether. A dimeric structure of formula $\{Li(Et_2O)Trip\}_2$ is observed when **1** is crystallized from ether solvent.[21] In this case the lithiums are coordinated to one ether and two Trip groups. The Li–C(ipso) distances are asymmetric with values of 2.249(3) and 2.203(3) Å. In addition, the coordination geometry surrounding the ipso carbons suggest that their interactions with the two bridging lithium centers are distinct with one primarily σ-bonding and the other having more π-character.

The synthesis of compound **2**, $\{Li(2,6\text{-}Mes_2C_6H_3)\}_2$, was carried out as part of a project to crystallize a monomeric, unsolvated, lithium organometallic derivative. Such a species has been characterized in the gas phase by electron diffraction; the compound $LiCH(SiMe_3)_2$ is a monomer (Li–C = 2.03(6) Å) in the vapor phase but is associated in the solid phase to form $[LiCH(SiMe_3)_2]_\infty$ which has an infinite (Li–C) backbone and Li–C distances in the range 2.14(3)–2.27(3) Å.[15] The ionic species $[Li(THF)_4][Li\{C(SiMe_3)_3\}_2]$[39] also contains a monomeric organolithium moiety. In this case, however, lithium is coordinated by two alkyl groups to afford an anion with a linear C–Li–C geometry and an Li–C bond length of 2.18(2) Å.

It was hoped that by using the bulky aryl group $2,6\text{-}Mes_2C_6H_3$, a neutral monomeric species of formula $Li(2,6\text{-}Mes_2C_6H_3)$, with a similar structure to that observed for the unique monomers $M(2,4,6\text{-}Ph_3C_6H_2)$ (M = Cu or Ag),[40] could be obtained. Instead a dimeric structure was observed for **2**. Presumably, the higher charge separation across the Li–C bond (in comparison to that in M–C (M = Cu or Ag)) results in a sufficient attractive force between the $Li^{\delta+}$–$C^{\delta-}$ dipoles to effect the association observed in **2**. In spite of this, there can be no doubt that the $2,6\text{-}Mes_2C_6H_3$ ligand is a very crowding one. For example, its thiolate derivative $HS(2,6\text{-}Mes_2C_6H_3)$ can effect quasi-two-coordination in the

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monomeric species $Fe\{S(2,6\text{-}Mes_2C_6H_3)\}_2$.[41] For **2** the primary interaction between the lithium and the organic groupsinvolves the ipso carbons, thereby generating a two-coordinate bent coordination geometry at the lithiums with Li–C distances in the range 2.16(1)–2.19(1) Å. The dimeric structure thus represents a model for the basic structural unit for a proposed structure of LiPh in the solid state.[34] The Li–C bond lengths are consistent with the low primary coordination of the lithium. There are further interactions between the lithium centers and the ipso carbons of the *o*-mesityl substituents. In the case of Li(1) and Li(1a) these interactions are Li(1)–C(21) = 2.51(1) Å and Li(1)–C(61) = 2.56(1) Å. For Li(2) the interactions are 2.57(1) Å (C(81)) and 2.56(1) Å (C(91)). The secondary bonding is thus different from, and much weaker than, that observed in **1** where there is an η^6-aromatic ring interaction. The secondary Li–C interactions are also weaker than those observed in $[Li(THF)C(SiMe_2Ph)_3]$[42] where the Li–C interaction also involves the ipso carbon from a phenyl ring. There is no structural evidence that the mesityl substituents interact strongly with the lithium centers since the angles surrounding the ortho carbons on the central phenyl ring (i.e. C(2), C(6), or C(8)) display little deviation from the idealized 120° values. The ^{13}C MMR spectrum of **2** displays the usual broad signal for the ipso carbon. The chemical shift, δ 173.5, is perhaps at a higher field (more shielded) than expected (cf. data for LiPh monomer, dimer, and tetramer). However, it should be noted that the ^{13}C NMR δ value for the ipso carbon in the monomeric $Li(Et_2O)_2(2,4,6\text{-}Ph_3C_6H_2)$ is 179.0.[23] Thus, it may be that the δ value of the ipso carbons in lithium aryls substituted by aryl rings differ markedly from unsubstituted species. There is no evidence from the bonding parameters of the ipso and ortho carbons that there is any significant charge delocalization in the central phenyl ring.

The compound **3** and the related species **3**·Mes*Br result from the treatment of Mes*Br with Li(*n*-Bu) in hexane. The isolation of such products indicates that the metal–halogen exchange reaction is incomplete under the reaction conditions described here. An alternative synthetic approach involving the reaction of Mes*Br or Mes*I with excess lithium powder in boiling hexane or toluene did not afford LiMes*. Instead, unreacted Mes*Br or Mes*I was recovered from the reaction mixture. In metal–halogen exchange reactions the lithium becomes attached to the more electronegative organic radical or the radical that forms the more stable carbanion. Thus, the lower EN of an alkyl radical versus an aromatic one generally drives the reaction illustrated in eq 1 to the right.

$$\mathrm{RLi} + \mathrm{ArX} \rightleftharpoons \mathrm{RX} + \mathrm{ArLi} \qquad (1)$$

$$(\mathrm{R = alkyl, Ar = aryl, X = halogen})$$

Among other factors (i.e. the nature of R, Ar, or X) the solvent can influence the reaction rate, the rate of exchange being greater in ether than in hydrocarbon solvents.[43] Since it was desired to prepare noncomplexed lithium aryls, hydrocarbons rather than ethers were used as solvents. Furthermore, the bulk of the aryl groups, especially in the case of **2** and **3**, probably retards the rate of exchange. Thus, in the case of **3**, after 2 days of stirring at room temperature in hexane only partial metal–halogen exchange was observed. It appears that substantial percentages of the reactants and products illustrated in eq 2

$$\mathrm{Li}(n\text{-Bu}) + \mathrm{Mes^{*}Br} \rightleftharpoons \mathrm{LiMes^{*}} + n\text{-BuBr} \qquad (2)$$

are present in the reaction mixture even after a prolonged reaction time. Cooling the solution affords crystals of **3** or **3**·Mes*Br in an overall yield of 36%. The isolation of **3** or **3**·Mes*Br rather than LiMes* from the reaction mixture is probably a consequence of the lower solubility of the former species.

The structure of **3** involves two distinct types of lithium coordination. The first type, which is observed at Li(2) and Li(4), involves an η^1-interaction with the α-carbon from an *n*-Bu group as well as an η^6-interaction with the Mes* aromatic ring. The other two lithiums (Li(1) and Li(3)) are η^1-bound to an ipso carbon from Mes* and are η^1-bound to an α-carbon from *n*-Bu. This results in an almost linear (C-Li(1 or 3)-C angles > 175°) coordination of these metals. However, it should be noted that Li(1) and Li(3) also interact with the ortho *tert*-butyl groups of Mes* with Li–C distances in the range 2.55(2)–2.66(2) Å. The Li(2) atom is almost centrally located over the C(23) ring (Li–C distances in the range 2.30(2) – 2.37(2) Å); however, Li(4) has much stronger interactions with the ipso carbon (Li(4)–C(1) = 2.28(2) Å) and the two ortho carbons than with the meta and para carbons, Li(4)–C(4) = 2.45(2) Å. Consistent with the low effective coordination number of the metals, the Li–C σ-bond distances fall within the range 2.03(3)–2.11(2) Å with an average value near 2.1 Å. These are on average shorter than the Li–C bond lengths (ca. 2.1–2.33 Å) observed in the solvates $[\{Li(n\text{-}Bu)\}_4TMEDA]_\infty$[44,45] or $\{Li(n\text{-}Bu)TMEDA\}_\infty$[44] or the species $[Li(n\text{-}Bu)\{LiO(t\text{-}Bu)\}]_4$[46] which have higher lithium coordination numbers. The structure of **3** resembles that observed for $(LiMes^*)_2\{LiP(H)Mes^*\}_2$. The use of a phosphido group instead of *n*-Bu results in some differences in structural detail; for example, whereas the η^1-Li–C and η^6-Li–C interactions have very similar distances in both compounds, the angle at the lithiums coordinated η^1 to the Mes* group is 144° in the phosphido species. This is in contrast to the almost linear arrangement observed for the corresponding lithium in **3**. In the ^{13}C NMR spectrum of **3**, the ipso-carbon peak of the phenyl ring was detected as a weak and broad singlet at δ 173.5. The ^{13}C signal of the α-carbon of the *n*-Bu was observed as a broad signal at 12.2 ppm. The ^7Li NMR spectrum displayed only one resonance, in spite of the fact that two separate lithium environments were observed in the X-ray crystal structure. It is possible that the two different lithium sites are in a rapid exchange which may also contribute to the broadening of the ipso ^{13}C signal.

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Supplementary Material Available: Tables of data collection parameters, bond distances and angles, hydrogen coordinates and anisotropic thermal parameters (36 pages); list of observed and calculated structure factors (65 pages). Ordering information is given on any current masthead page.

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