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Synthesis and structure of two lithium terphenyls and a "halide rich" terphenyl lithium species

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Abstract

The syntheses and characterization of two new terphenyl iodides 2,6-(2,3,4,5,6-$Me_5C_6)_2C_6H_3I$ ($Ar^{Pmp_2}I$) and 2,6-(3,5-$Bu^t_2C_6H_3)_2C_6H_3I$ ($Ar^{Dbp_2}I$) are described. Treatment of these with $LiBu^n$ or $LiBu^t$ afforded their lithium salts $[Ar^{Pmp_2}Li]_2$ (**2**), $Ar^{Dbp_2}\{Li(OEt_2)\}_2I$ (**3**), and $[Ar^{Dbp_2}Li]_2$ (**4**), which were spectroscopically characterized. The X-ray crystal structures of **2** and the "halide-rich" species **3** as well as that of the previously known $[2,6\text{-}(2,6\text{-}Me_2C_6H_3)_2C_6H_3Li]_2$ (i.e. $[Ar^{Xyl_2}Li]_2$, **1**) were determined. The structures of both **1** and **2** are dimers in which the lithiums bridge the *ipso* carbons of the central aryl ring of each terphenyl ligand and also interact with the *ipso* carbons of the flanking aryl rings. The structure of **3** is a rare example of a structurally characterized "halide rich" organolithium complex and has a monomeric arrangement in which two ether-coordinated lithiums are bridged by an *ipso*-carbon of the central aryl ring as well as an iodine atom.
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1. Introduction

Organolithium compounds are widely used in chemical reactions due to their ease of synthesis, higher reactivity, and greater versatility than Grignard reagents [1]. There is much interest in their structures due to their electron deficient character [2] as a result of which they form aggregates and/or complexes with Lewis bases or donor solvents. If lithium is attached to a bulky ligand, however, both of these processes are minimized for steric reasons. Over the past decade, *meta*-terphenyl ligands have been increasingly used as very crowding ligands that can stabilize compounds with unusual bonding and structures [3] as well as building blocks for macromolecules [4]. The lithium derivatives of these large aryls are the most widely used transfer agents, and their crystal structures have shown that their aggregation numbers are lower than the typically found four or six due to their steric bulk [3]. For example, monomeric terphenyl lithium structures can be stabilized with use of one or two ethers, THFs, or a benzene donor molecule as in 2,4,6-$Ph_3C_6H_2Li(OEt_2)_2$ [5], 2,6-$Ph_2C_6H_3Li(OEt_2)_2$ [6], 2,6-(1-Naph)$_2C_6H_3Li(THF)_2$ (Naph = $C_{10}H_7$) [7], 2,6-(4-$MeOC_6H_4)_2C_6H_3Li(OEt_2)_2$ [8], 2,6-(4-^{t}Bu$C_6H_4)_2C_6H_3Li(OEt_2)_2$ [9], 2,6-(2,6-^{i}Pr$_2$-4-^{t}Bu)$_2C_6H_3Li(OEt_2)$ [10], 2,6-Trip$_2C_6H_3Li(OEt_2)$ (Trip = 2,4,6-^{i}Pr$_3C_6H_2$) [11], or 2,6-Trip$_2C_6H_3Li(\eta^6$-$C_6H_6)$ [12]. Currently, two types of base free dimeric structures are known. One features the lithiums bridging *ipso* carbons from a central phenyl ring as in [2,6-Mes$_2$-$C_6H_3Li]_2$ (Mes = 2,4,6-$Me_3C_6H_2$); i.e. $[Ar^{Mes_2}Li]_2$ [13], where the lithiums also interact with the *ipso* carbons of a flanking ring. The second structural type involves a Li–C(*ipso*) σ-interaction to a central aryl ring, in addition to an $\eta^6\pi$-interaction with a flanking aryl ring on the other terphenyl group of the dimer as in

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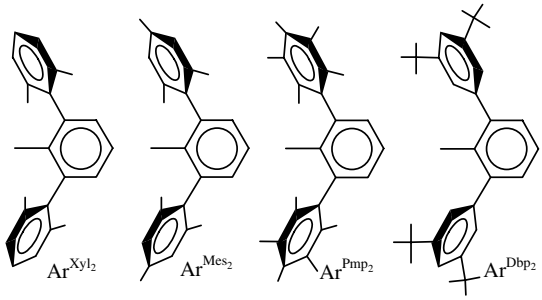
[2,6-Dipp$_2$C$_6$H$_3$Li]$_2$ (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$); i.e. [Ar^{Dipp_2}Li]$_2$ [12]. In addition there exist Lewis base/solvent stabilized dimeric complexes as in the mono solvated, 2,6-[Ph$_2$C$_6$H$_3$Li]$_2$(THF) [7]. Other known structures are the mixed lithium terphenyl/lithium alkyl [2,6-Trip$_2$-C$_6$H$_3$Li(^{t}BuLi)]$_2$ [9]; i.e. [Ar^{Trip_2}Li(Bu^{t}Li)] as well as the *ortho*-metallated derivative, [LiC$_6$H$_3$-2-C$_6$H$_3$-2-Me-5-^{t}Bu)-6-(C$_6$H$_3$-2-CH$_2$Li-5-^{t}Bu)]$_2$ [9]. Additionally, a dimeric intramolecularly Lewis base coordinated [2,6-(2-MeOC$_6$H$_4$)$_2$C$_6$H$_3$Li(THF)LiI]$_2$ which includes two equivalents of lithium iodide [14] has been characterized. We now report the structure of [2,6-(2,6-Me$_2$C$_6$H$_3$)$_2$C$_6$H$_3$Li]$_2$, [Ar^{Xyl_2}Li]$_2$ (**1**) and the synthesis and structure of [2,6-(2,3,4,5,6-Me$_5$C$_6$)$_2$C$_6$H$_3$Li]$_2$, [Ar^{Pmp_2}Li]$_2$ (**2**), which exist as dimers that resemble the previously reported [Ar^{Mes_2}Li]$_2$ [13]. In addition, the synthesis and structure of [2,6-(3,5-^{t}Bu$_2$C$_6$H$_3$)$_2$-C$_6$H$_3$]{Li(OEt)$_2$}$_2$I, [Ar^{Dbp_2}{Li(OEt)$_2$}$_2$I] (**3**), which is a rare example [14–16] of a structurally characterized "halide rich" organometallic species are described.



2. Experimental

2.1. General procedures

All experiments were carried out by using modified Schlenk techniques under an Argon atmosphere or in a Vacuum Atmospheres HE-43 dry box. All solvents were distilled from Na/K alloy and degassed twice before use. The lithium reagents Bu^{n}Li (1.6 M solution in hexanes or 2.5 M solution in hexanes) and Bu^{t}Li (1.5 M solution in hexanes) were purchased commercially and used as received. 1-Bromo-3,5-di-*tert*-butyl-benzene was prepared by a known literature procedure [17]. 1-Bromo-2,3,4,5,6-penta methyl-benzene and 1-bromo-2,6-dimethyl-benzene were purchased commercially and used as received. ^{1}H and ^{13}C NMR spectroscopic data were recorded on a Varian 300 MHz instrument and referenced to the deuterated solvent.

2.2. [Ar^{Xyl_2}Li4]$_2$ (1)

Ar^{Xyl_2}I [18] (6.14 g, 14.89 mmol) was dissolved in hexane (60 mL) and cooled to ca. 0 °C in an ice bath for 30 min. Bu^{n}Li (10.2 mL of a 1.6-M solution in *n*-hexane) was added to the aryl iodide solution via syringe with rapid stirring. The solution was allowed to warm to room temperature and was stirred overnight. The resultant precipitate was allowed to settle and the supernatant liquid was decanted via cannula. The precipitate was washed with hexane (30 mL) and supernatant liquid was decanted. The remaining product **1** was isolated as a white powder and dried under reduced pressure. Yield: 3.26 g, 75%. m.p. 169–172 °C. ^{1}H NMR (C$_6$D$_6$; 300 MHz): δ 1.76 (s, 12H, CH_3); δ 6.74 (d, 2H, $^3J_{HH}$ = 7.20 Hz; *m*-C$_6$H$_3$); δ 6.945 (d, 4H, $^3J_{HH}$ = 7.20 Hz; *m*-Xyl); 7.12 (t, 2H, $^3J_{HH}$ = 7.20 Hz; *p*-Xyl); δ 7.18 (t, 1H, $^3J_{HH}$ = 7.20 Hz; *p*-C$_6$H$_3$); ^{13}C NMR (C$_6$D$_6$; 75.4 MHz): δ 21.73 (C_3); δ 123.54 (*p*-Xyl); δ 126.29 (*p*-C$_6$H$_3$); δ 127.33 (*m*-Xyl); δ 128.92 (*o*-Xyl); δ 136.28 (*m*-C$_6$H$_3$); δ 146.34 (*o*-C$_6$H$_3$); δ 151.89 (*i*-Xyl); δ 172.66 (*i*-C$_6$H$_3$). Colorless crystals of **1** that were suitable for X-ray crystallography were obtained by dissolving the colorless powder in 40 mL of benzene and reducing the volume to 15 mL. The solution was cooled in the refrigerator for 2 weeks at ca. 6 °C to afford large colorless crystals of **1**.

2.3. [Ar^{Pmp_2}Li]$_2$ (2)

In a 500-mL 3-neck flask, a solution of 1,3-dichlorobenzene (7.34 g, 0.050 mol) in THF (100 mL) was cooled to −78 °C in a dry ice/acetone bath. *n*-BuLi (31.25 mL of a 1.6-M solution in *n*-hexane) was added dropwise via cannula during a period of 20 min. The formation of a white precipitate was observed and stirring was continued for 1 h at −78 °C. A solution of pentamethylphenyl magnesium bromide in 100 mL of THF, freshly prepared from Mg (2.66 g, 0.109 mol) and pentamethyl-bromo-benzene (22.79 g, 0.100 mol) was added at −78 °C over a period of 1 h. The solution was allowed to warm to room temperature and stirring was continued overnight. The resulting brown solution was heated to reflux for 2.5 h. After cooling the reaction mixture in an ice bath for 1.5 h, iodine (17.0 g, 0.067 mol) was added and the suspension was rapidly stirred overnight. The excess iodine was destroyed with Na$_2$SO$_3$ solution and the aqueous layer was separated and washed three times with ether. The organic layers were then combined, and the solvent was evaporated, and the residue was dried under reduced pressure. All of the volatile side products were then removed by distillation. Ethanol (300 mL) was added to the residue and the mixture was heated to reflux overnight. After the mixture was cooled to room temperature, it was filtered and the pale yellow solid was washed with methanol and dried. Yield: 8.80 g, 35.3%. m.p. 168–170 °C. ^{1}H NMR (CDCl$_3$; 300 MHz): δ 1.98 (s, 12H, *o*-CH_3); δ 2.30 (s, 12H, *m*-CH_3); δ 2.35 (s, 6H, *p*-CH_3); δ 7.08 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *m*-C$_6$H$_3$); δ 7.46 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *p*-C$_6$H$_3$). ^{13}C NMR (CDCl$_3$; 75.4 MHz): δ 16.88

(*o*-CH_3); δ 17.2{^{1}H} (*p*-CH_3); 18.00 (*m*-CH_3); δ 109.08 (*i*-C_6H_3); δ 127.78 (*o*-*Pmp*); δ 128.57 (*o*-C_6H_3); δ 130.92 (*m*-C_6H_3); δ 132.31 (*p*-C_6H_3); δ 134.35 (*m*-*Pmp*); δ 142.86 (*i*-*Pmp*); δ 148.88 (*p*-*Pmp*).

$Ar^{Pmp_2}I$ (3.24 g, 6.52 mmol) was dissolved in hexane (60 mL) and cooled to 0 °C in an ice bath for 30 min. Bu^nLi (2.75 mL of a 2.5-M solution in *n*-hexane) was added to solution via syringe with rapid stirring. The solution was allowed to warm to room temperature and was stirred overnight. The precipitate was allowed to settle and the supernatant liquid was removed via cannula. The precipitate was washed with cold hexane (30 mL) after which it was allowed to settle. The supernatant hexane was decanted and the product **2** was obtained as a white powder. Yield: 1.595 g, 65%. m.p. 178–181 °C. ^{1}H NMR (C_6D_6; 300 MHz): δ 1.83 (s, 12H, *o*-CH_3); δ 2.09 (s, 12H, *p*-CH_3); δ 2.14 (s, 6H, *m*-CH_3); δ 6.78 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *m*-C_6H_3); δ 7.20 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *p*-C_6H_3). ^{13}C NMR (C_6D_6; 75.4 MHz): δ 16.74 (*p*-CH_3); δ 17.24 (*o*-CH_3); 18.06 (*m*-CH_3); δ 124.40 (*o*-*Pmp*); δ 126.11 (*o*-C_6H_3); δ 131.76 (*m*-C_6H_3); δ 132.87 (*p*-C_6H_3); δ 133.70 (*m*-*Pmp*); δ 144.60 (*i*-*Pmp*); δ 154.22 (*p*-*Pmp*); δ 174.79 (*i*-C_6H_3). Colorless crystals of **2** were obtained by dissolving the colorless powder in toluene/hexane mixture (30 mL/10 mL), reducing the volume to ca. 10 mL, and cooling in a freezer for 4 days at −13 °C.

2.4. $[Ar^{Dbp_2}\{Li(OEt)_2\}_2]$ (**3**)

The aryl iodide $Ar^{Dbp_2}I$ was prepared in a similar manner to the that described for $Ar^{Pmp_2}I$ and $Ar^{Trip_2}I$ [18] with use of 1,3-dichlorobenzene (13.5 g, 0.0918 mol) in THF (200 mL); *n*-BuLi (39 mL of a 2.5-M solution in *n*-hexane)and a solution of 3,5-di-*tert*-butylphenyl magnesium bromide in 400 mL of THF, freshly prepared from Mg (6.130 g, 0.252 mol), and 1-bromo-3,5-di-*tert*-butylbenzene (54.5 g, 0.202 mol). Work up in the same manner afforded the product $Ar^{Dbp_2}I$ as an off-white powder. Yield: 35 g (65%). m.p. 179–181 °C. ^{1}H NMR (C_6D_6; 300 MHz): δ 1.323 (s, 36H, C(CH_3)$_3$); δ 7.074 (t, 1H, $^3J_{HH}$ = 7.60 Hz; *p*-C_6H_3); δ 7.225 (d, 2H, $^3J_{HH}$ = 7.60 Hz; *m*-C_6H_3); 7.425 (d, 4H, $^4J_{HH}$ = 1.6 Hz; *o*-Ar^{Dbp_2}); δ 7.561(t, 2H, $^4J_{HH}$ = 1.6 Hz; *p*-Ar^{Dbp_2}); ^{13}C NMR (C_6D_6; 75.4 MHz): δ 31.58 (C(CH_3)$_3$); δ 34.94 (*C*(CH_3)$_3$); δ 105.13 (*i*-C_6H_3); δ 121.09 *p*-Ar^{Dbp_2}); 124.41 (*o*-Ar^{Dbp_2}); δ 128.14 (*p*-C_6H_3); δ 128.83 (*m*-C_6H_3); 145.50 (*o*-C_6H_3); δ 149.66 (*i*-Ar^{Dbp_2}); δ 150.32 (*m*-Ar^{Dbp_2}).

Bu^tLi (14.25 mmol, 9.5 mL of a 1.5 M solution) was added dropwise via syringe to $Ar^{Dbp_2}I$ (4.04 g, 6.96 mmol) in hexane (50 mL) and diethyl ether (10 mL), and at ca. −78 °C with rapid stirring. After 30 min, the slurry was allowed to warm to room temperature and stirred overnight. The volatile solvent was removed under reduced pressure. The residue was extracted with 50 mL of hexane and filtered through Celite. The colorless filtrate was concentrated to incipient crystallization (ca. 10 mL) and stored in a ca.−20 °C freezer to afford **3** as colorless crystals. Yield: 3.88 g, 75%. m.p. 239–240 °C (sweats 203 °C). ^{1}H NMR (C_6D_6; 300 MHz): δ 0.67 (t, 6H, $^3J_{HH}$ = 6.8 Hz, O(CH_2C H_3)$_2$); δ 1.22 (s, 18H, C(CH_3)$_3$); δ 1.32 (s, 9H, C(CH_3)$_3$); δ 1.51 (s, 9H, C(CH_3)$_3$); δ 2.99 (q, 4H, $^3J_{HH}$ = 6.8 Hz, O(CH_2CH_3)$_2$); δ 7.25 (t, 1H, $^4J_{HH}$ = 2.0 Hz, *p*-Ar^{Dbp_2}); δ 7.47 (t, 1H, $^3J_{HH}$ = 7.2 Hz, *p*-C_6 H_3); δ 7.57 (t, 1H, $^4J_{HH}$ = 2.0 Hz, *p*-Ar^{Dbp_2}); δ 7.61 (d, 2H, $^4J_{HH}$ = 2.0 Hz, *o*-Ar^{Dbp_2}); δ 7.65 (t, 1H, $^4J_{HH}$ = 2.0 Hz, *o*-Ar^{Dbp_2}); δ 7.79 (d, 2H, $^3J_{HH}$ = 7.2 Hz, *m*-C_6H_3). ^{13}C NMR (C_6D_6; 75.4 MHz): δ 14.21 (O(CH_2CH_3)$_2$); δ 31.75 (C(CH_3)$_3$); δ 35.04 (*C*(CH_3)$_3$); δ65.73 (O(CH_2CH_3)$_2$); δ 120.93 (*o*-Ar^{Dbp_2}); δ 121.43 (*o*-Ar^{Dbp_2}); δ 122.00 (*p*-Ar^{Dbp_2}); δ 122.28 (*p*-Ar^{Dbp_2}); δ 125.29 (*p*-C_6H_3); δ 126.60 (*m*-C_6H_3); 146.60 (*o*-C_6H_3); δ 151.99 (*i*-Ar^{Dbp_2}); δ 153.29 (*m*-Ar^{Dbp_2}); δ 153.35 (*m*-Ar^{Dbp_2}); δ 174.62 (*i*-C_6H_3).

2.5. $[Ar^{Dbp_2}Li]_2$ (**4**)

$Ar^{Dbp_2}I$ (5.80 g, 9.99 mmol) was dissolved in hexane (65 mL) and cooled to ca. 0 °C with rapid stirring. Bu^nLi (4.00 mL of a 2.5-M solution in *n*-hexane) was added to solution via syringe. The solution was allowed to warm to room temperature and stirred overnight. The precipitate was allowed to settle and the supernatant liquid was decanted via cannula. The precipitate was washed with hexane (30 mL) and supernatant liquid was decanted to yield a white powder. Compound **4** was not crystallized despite numerous attempts. Yield: 3.91 g, 85%. m.p. 185–187 °C. ^{1}H NMR (C_6D_6; 300 MHz): δ 1.22 (s, 36H, C(CH_3)$_3$); δ 7.25 (t, 2H, $^4J_{HH}$ = 2.0 Hz, *p*-Ar^{Dbp_2}); δ 7.47 (t, 1H, $^3J_{HH}$ = 7.60 Hz, *p*-C_6H_3); 7.65 (d, 4H, $^4J_{HH}$ = 2.0 Hz, *o*-Ar^{Dbp_2}); δ 7.80 (d, 4H, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_3). ^{13}C NMR (C_6D_6; 75.4 MHz): δ 31.91 (C(CH_3)$_3$); δ 35.16 (*C* (CH_3)$_3$); δ 121.06 (*o*-Ar^{Dbp_2}); δ 122.43 (*p*-Ar^{Dbp_2}); δ 125.59 (*p*-C_6H_3); δ 126.88 (*m*-C_6H_3); 146.85 (*o*-C_6H_3); δ 152.33 (*i*-Ar^{Dbp_2}); δ 153.42 (*m*-Ar^{Dbp_2}); δ 175.14 (*i*-C_6H_3).

2.6. X-ray data collection solution and refinement

Crystals of **1**–**3** were coated with hydrocarbon oil, mounted on a glass fiber and placed in the N_2 cold stream on the diffractometer as previously described [19]. All data were obtained using a Bruker SMART 1000 diffractometer and Mo Kα radiation. The SHELXTL version 5.03 program package was used for the structure solutions and refinements [20]. Absorption corrections were applied using the SADABS program [21]. The structures were solved by direct methods and refined by full matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms

Table 1
Crystallographic data for **1**, **2** and **3a**

	1	**2**	**3**
Formula	$C_{44}H_{42}Li_2$	$C_{56}H_{66}Li_2$	$C_{42}H_{65}ILi_2O_2$
Fw	584.66	752.97	742.72
Color, habit	Colorless, prisms	Yellow, blocks	Colorless, plates
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$I4_1/a$	$C2/c$	$P2_1/n$
a (Å)	20.5829(4)	17.2305(19)	15.7699(5)
b (Å)	20.5829(4)	14.7246(16)	10.4163(3)
c (Å)	21.7619(13)	17.6380(19)	25.7460(8)
α (°)	90.0	90	90.0
β (°)	90.0	91.355(2)	91.6860(10)
γ (°)	90.0	90.0	90.0
V (Å^3)	13456.1(7)	4473.7(8)	4227.3(2)
Z	16	4	4
d_{calc} (Mg/m^3)	1.154	1.118	1.167
θ Range (°)	1.98–27.50	1.82–26.00	2.11–27.48
μ (mm^{-1})	0.064	0.062	0.788
Observed data $I > 2\sigma(I)$	5361	3614	8176
R_1 (obs data)	0.0677	0.0420	0.0276
wR_2 (all data)	0.1480	0.1125	0.0686

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**3**

1		**2**		$[Ar_2^{Mes}Li]_2$		**3**	
Li(1)–C(1)	2.161(6)	Li(1)–C(1)	2.176(2)	Li(1)–C(1)	2.17(1)	Li(1)–C(1)	2.156(4)
Li(1)–C(31)	2.143(5)	Li(1)–C(18)	2.6933(17)	Li(1a)–C(1)	2.16(1)	Li(2)–C(1)	2.172(4)
Li(1)–C(15)	2.579(7)	Li(1)–C(2)	2.7219(13)	Li(1a)–C(6)	2.70(1)	Li(1)–I(1)	2.751(3)
Li(1)–C(45)	2.630(5)	Li(2)–C(1)	2.230(2)	Li(1)–C(21)	2.51(1)	Li(2)–I(1)	2.738(3)
Li(1)–C(32)	2.691(5)	Li(2)–C(7)	2.4845(17)	Li(1a)–C(61)	2.56(1)	Li(1)–C(7)	2.578(4)
Li(1)–C(2)	2.693(6)	Li(2)–C(6)	2.7298(13)	Li(2)–C(7)	2.20(1)	Li(2)–C(21)	2.669(4)
Li(2)–C(1)	2.187(6)	Li(1)···Li(2)	2.331(5)	Li(2)–C(8)	2.73(1)	Li(1)–O(1)	1.907(3)
Li(2)–C(7)	2.599(5)			Li(2)–C(11)	2.19(1)	Li(2)–O(2)	1.902(4)
Li(2)–C(31)	2.186(5)			Li(2)–C(91)	2.56(1)	C(1)–C(2)	1.423(2)
Li(2)–C(37)	2.631(5)	Li(1)–C(1)–Li(2)	63.87(11)	Li(2)–C(12)	2.70(1)	C(1)–C(6)	1.417(2)
Li(2)–C(42)	2.701(6)	Li(1)—C(1)–C(2)	96.30(11)	Li(1)···Li(1a)	2.27(2)	Li(1)···Li(2)	2.664(5)
Li(2)–C(7)	2.599(5)	Li(2)–C(1)–C(6)	94.07(10)	Li(2)···Li(2a)	2.31(2)		
Li(2)–C(37)	2.631(5)	C(1)–Li(1)–C(1A)	118.39(17)				
Li(1)···Li(2)	2.300(7)	C(1)–Li(2)–C(1A)	113.86(15)			C(1)–Li(1)–I(1)	112.96(13)
		C(2)–C(1)–C(6)	113.64(11)	Li(1)–C(1)–Li(1a)	63.2(5)	C(1)–Li(2)–I(1)	112.90(14)
				C(1)–Li(1)–C(1a)	116.8(5)	Li(1)–C(1)–Li(2)	75.97(13)
Li(1)–C(1)–Li(2)	63.85(19)			C(21)–Li(1)–C(1a)	146.1(5)	Li(1)–C(1)–C(6)	139.36(16)
Li(1)–C(1)–C(2)	95.5(3)			C(21)–Li(1)–C(1)	64.4(3)	Li(2)–C(1)–C(2)	94.36(15)
Li(2)–C(1)–C(6)	98.2(3)			C(61a)–Li(1)–C(1a)	64.1(3)	Li(1)–I(1)–Li(2)	58.08(9)
C(1)–Li(1)–C(31)	117.4(2)			C(61a)–Li(1)–C(21)	134.1(5)		
C(1)–Li(2)–C(31)	114.5(2)			C(2)–Li(1)–C(1a)	143.1(5)		
C(2)–C(1)–C(6)	113.9(3)			C(7)–Li(2)–C(11)	116.5(5)		
Li(1)–C(31)–Li(2)	64.17(18)			C(81)–Li(2)–C(11)	145.0(5)		
				C(81)–Li(2)–C(7)	143.4(3)		

Data for $[Ar_2^{Mes}Li]_2$ have been included for comparison.

were included in the refinement at calculated positions using a riding model included in the SHELXTL program package. Some details of the data collection and refinement are given in Table 1. Selected bond distances and angles for **1**–**3** are provided in Table 2. The *t*-Bu groups in the structure of **3** are disordered such that the methyl groups occupy two positions with 48% and 52% occupancies. The disordered carbons were refined isotropically for simplicity.

3. Discussion

3.1. Synthesis

The compounds **1**–**3** were obtained by the reaction of one or two equivalents of alkyl lithium (Bu^{n}Li or Bu^{t}Li) with the corresponding terphenyl iodide derivative. These iodide precursors were synthesized by modification of the one-pot synthesis of terphenyl iodides [18].

The metal–halogen exchange route to the lithium terphenyl is an adaptation of the Schlosser method [22] (using *n*-butyl lithium) and has been used to obtain lithium terphenyl compounds since 1991 [5]. This reaction originally involved the use of 1 equiv. of *n*-butyl lithium with the terphenyl iodide as shown in Eq. (1) [5].

$$1\text{-IC}_6\text{H}_2\text{-}2,4,6\text{-PH}_3 \overset{n\text{-BuLi}}{\rightleftharpoons} \text{LiC}_6\text{H}_2\text{-}2,4,6\text{-Ph}_3 + n\text{-BuI} \quad (1)$$

Further experiments showed that the Seebach method [23] (using the more reactive *tert*-butyl lithium) afforded higher yields of the very crowded lithium terphenyl, 1-IC_6H_3-2,6-$Trip_2$, as seen in Eq. (2).

$$1\text{-IC}_6\text{H}_3\text{-}2,6\text{-Trip}_2 \underset{\text{Et}_2\text{O}}{\overset{2t\text{-BuLi}}{\rightleftharpoons}} (\text{Et}_2\text{O})\text{LiC}_6\text{H}_3\text{-}2,6\text{-Trip}_2 + \text{LiI} + t\text{-BuH} + (\text{CH}_3)\text{CHCH}_2 \quad (2)$$

The addition of a second equivalent of tert-butyl lithium displaces the equilibrium to the right so that the reaction proceeds to completion. For the synthesis of compounds **1** and **2**, it was found that the original synthesis involving the use of 1 equiv. of Bu^nLi afforded the products in good yield.

$$\begin{matrix} \text{Ar}^{\text{Xyl}_2}\text{I} \\ \text{-or-} \\ \text{Ar}^{\text{Pmp}_2}\text{I} \end{matrix} \overset{n\text{-BuLi}}{\rightleftharpoons} \begin{matrix} [\text{Ar}^{\text{Xyl}_2}\text{Li}]_2 & \mathbf{1} \\ \text{-or-} & \\ [\text{Ar}^{\text{Pmp}_2}\text{Li}]_2 & \mathbf{2} \end{matrix} + n\text{-BuI} \quad (3)$$

The use of Bu^nLi also sufficed to obtain the salt $[Ar^{Dbp_2}Li]_2$ (**4**) which contains Bu^t groups in the *meta* positions of the flanking aryl rings. Previous attempts to synthesize the more crowded *ortho* Bu^t substituted terphenyl 1-IC_6H_3-2,6-$(C_6H_2\text{-}2,4,6\text{-}Bu^t_3)_2$ were unsuccessful presumably for steric reasons [11]. In the *meta*-Bu^t substituted salt **3**, however, the steric pressure is sufficiently relaxed to allow its isolation in good yield.

The synthesis of **3** arose from the inability to grow crystals of **4** that were suitable for X-ray crystallography. This prompted experiments that involved different solvents and reagent stoichiometries. Thus the unusual 'halide rich' adduct, **3**, could be synthesized by using the Seebach method, in which two equivalents of *t*-butyl lithium were reacted with the terphenyl iodide at −78 °C in a hexane/diethyl ether solution, Eq. (4).

$$\text{Ar}^{\text{Dbp}_2}\text{I} \underset{\text{Et}_2\text{O},-78^\circ\text{C}}{\overset{2t\text{-BuLi}}{\rightleftharpoons}} \text{Ar}^{\text{Dbp}_2}\{\text{Li}(\text{OEt}_2)_2\}\text{I} \quad \mathbf{3} + t\text{-BuH} + (\text{CH}_3)\text{CHCH}_2 \quad (4)$$

The species **3** differs from the product in Eq. (2) in that the LiI is not eliminated in this case. It seems that the greater steric demand of the – C_6H_3-$Trip_2(Ar^{Trip_2})$ ligand in comparison to that of – Ar^{Dbp_2} does not permit the formation of the ether complexed LiI adduct seen in **3**.

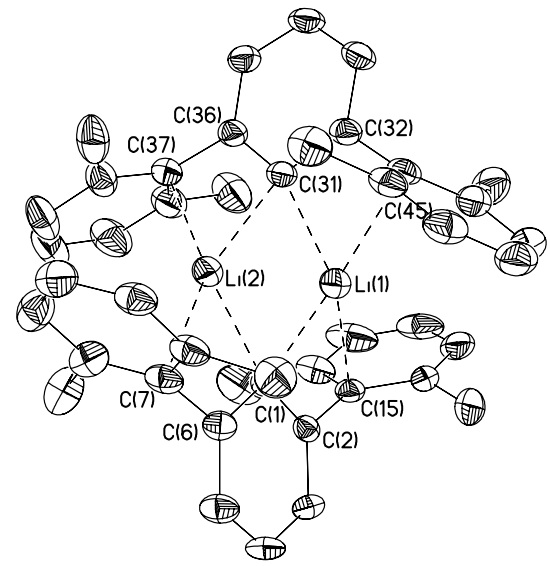


Fig. 1. Thermal ellipsoid plot (50%) of **1**. Hydrogen atoms are not shown for clarity.

The ^{13}C NMR spectra of **1**–**4** display characteristic chemical shifts below 170 ppm for the lithiated *ipso* carbons. These broad signals were observed at δ 172.66 ppm (**1**), 174.79 ppm (**2**), 174.62 ppm (**3**), and 175.14 ppm (**4**) are comparable to the 173.55 ppm reported for $[Ar^{Mes_2}Li]_2$ [13].

3.2. Structures

The structure of **1** which is illustrated in Fig. 1, consists of dimeric $[Ar^{Xyl_2}Li]_2$ units that have no crystallographically imposed symmetry. The lithiums bridge the terphenyl groups almost symmetrically and interact primarily with the *ipso* carbons of the central aryl rings to afford a planar Li_2C_2 core. This creates a quasi two-coordinate bent geometry (bending angles C(1)–Li(1)–C(31) = 117.4(2)° and C(1)–Li(2)–C(31) = 114.5(2)°) at the lithium atoms. The Li–C distances range 2.143(5)–2.187(6) Å, but there are further weaker interactions between the lithium centers and the *ipso* carbons of the *o*-xylyl substituents. These Li···C distances are ca. 0.4 Å longer than those to the *ipso* carbons of the central rings and have the values Li(1)–C(15) = 2.579(7) Å, Li(1)–C(45) = 2.630(5) Å, Li(2)–C(7) = 2.599(5) Å, and Li(2)–C(37) = 2.631(5) Å.

The structure of **2** (Fig. 2) is broadly similar to that of **1**. However, in this case, there is a crystallographically required axis of symmetry along the Li(1)···Li(2) vector. As in **1**, the lithiums interact most strongly with the *ipso* carbons of the central aryl rings of each Ar^{Pmp_2} group (Li(1)–C(1) = 2.176(2) and Li(2)–C(1) = 2.230(2) Å) to produce a planar $Li_2\{C(ipso)\}_2$ core in which the bending angles at the lithiums are 118.4(2)° at Li(1) and 113.9(2)° at Li(2) which are within 1° of the correspond-

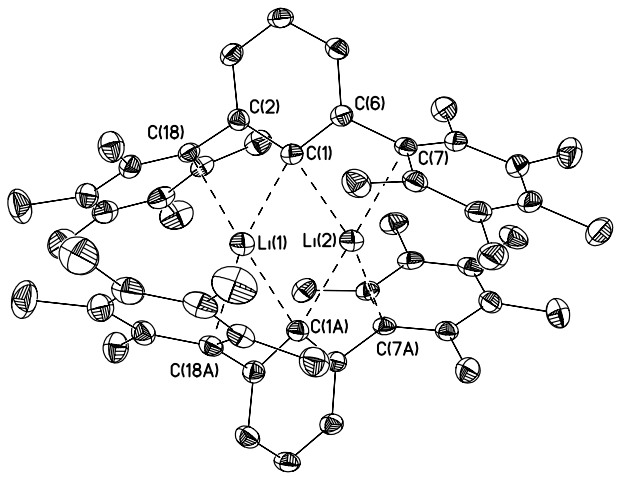


Fig. 2. Thermal ellipsoid plot (50%) of **2**. Hydrogen atoms are not shown for clarity.

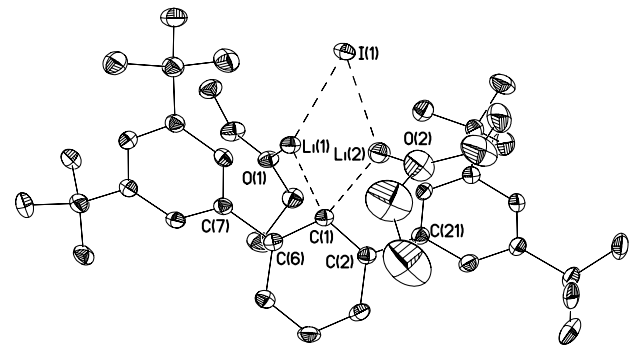


Fig. 3. Thermal ellipsoid plot (50%) of **3**. Hydrogen atoms are not shown for clarity.

ing angles in **1**. In addition there are secondary interactions between each lithium and the flanking aryl rings as illustrated in Fig. 2 which have values of 2.693(2) Å to C(18) and 2.485(2) Å to C(7).

The major differences between the structures of **1** and **2** reflect the increased steric crowding of the flanking aryl substituents in **2**. This results in longer Li–C(*ipso*) distances to the central aryl (avg. 2.20 Å) in **2** in comparison to than those (avg. 2.17 Å) observed in **1**. The average Li–C distance observed in $[Ar^{Mes_2}Li]_2$, which lies between **1** and **2** in terms of steric crowding, is 2.18 Å. The fact that this lies between the average for **1** and **2** is probably fortuitous since the standard deviations for this structure are relatively high (Table 2). The "tighter" structure of **1** induces a closer approach of the terphenyl ligands across the molecule and this is reflected in the higher dihedral angle between the central aryl rings: 81.4° in **1** versus 64.9° in **2**.

An unusual feature of the structures of both **1** and **2** is that one lithium is more strongly bound than the other. Thus, in **1**, Li(1) has distances of 2.143(5) and 2.161(6) Å to the central *ipso* carbons C(1) and C(31) whereas the corresponding distances for Li(2) are 2.186(5) and 2.187(6) Å. In **2**, there is a similar pattern where the Li(1)–C(1) and Li(2)–C(1) bond lengths are 2.176(2) and 2.230(2) Å. There is no corresponding pattern in the secondary Li–C interactions, however, and the average Li–C interactions to the *meta* carbon of the central ring and the *ipso* carbon of the flanking ring are very similar.

The structure of **3** is shown in Fig. 3. It consists of $[Ar^{Dbp_2}\{Li(OEt)_2\}_2I]$ units with no symmetry requirement. The *ipso* carbon of the central aryl rings is bound to two ether solvated lithiums which are also bridged by iodine. The core of the molecule comprises a planar Li_2-C(*ipso*)I unit which subtends a dihedral angle of 48.1° with respect to the plane of the central aryl ring. The Li–C bond lengths average 2.164 Å, which is very similar to that observed in **1**. The Li–O bonds (avg. 1.905 Å) are slightly shorter than those observed in other three coordinate terphenyl etherate complexes: 2,4,6-$Ph_3C_6H_2Li(OEt_2)_2$ [5] (avg. 1.962 and 1.931 Å); 2,6-$Ph_2C_6H_3Li(OEt_2)_2$[6] (1.944 Å); 2,6-(4-$MeOC_6H_4)_2$-$C_6H_3Li(OEt_2)_2$ [8] (1.954 Å), 2,6-(4-$^tBuC_6H_4)_2$-$C_6H_3Li(OEt_2)_2$ [9] (1.950 Å), but are longer than those in 2,6-(2,6-$^iPr_2$-4-$^tBu)_2C_6H_3Li(OEt_2)$ [10] (1.881 Å); and 2,6-$Trip_2C_6H_3Li(OEt_2)$ [11] (1.850 Å) where the lithium is two coordinate. The Li–I distances (2.738(3) and 2.751(3) Å) also resemble those observed in the complex $[2,6\text{-}(2\text{-}MeOC_6H_4)_2C_6H_3Li(THF)LiI]_2$ [14], where the Li–I distance are 2.760 and 2.820 Å. The lithium centers are formally three coordinate and are bound to the *ipso* carbon of the central ring, an ether oxygen and iodine. However, inspection of the structural data shows that the coordination to these ligands is not planar as indicated by the sums of the interligand angles at the lithiums of 346.6° (Li(1)) and 350.8 (Li(2)). These deviations from planarity are due to further weak interactions between the lithiums and carbons from the flanking aryl rings. The closest such interactions involve the ring *ipso* and *ortho* carbon atoms and fall in the range 2.578(2)–2.685(4) Å. The Li(1)···Li(2) separation (2.664(5) Å) is more than 0.3 Å longer than those observed in **1** and **2**. This difference is probably due to the very narrow Li–C(*ipso*)–Li angles (ca. 64°) imposed by the quasi-two coordinate lithium centers in **1** and **2** which involve wide C(*ipso*)–Li–C(*ipso*) angles. In **3**, however, the lithiums are quasi three coordinate; in addition, a very narrow Li–I–Li angle of 58.08(9)° is observed at the relatively sterically unencumbered iodine. These factors permit a wider Li–C(*ipso*)–Li angle (75.97(13)°) and hence a longer Li···Li separation to be observed.

The structure of **3** is a rare instance of a structurally characterized "halide rich" organolithium species [14–18]. Cubane structures have been observed in the case of $(Et_2O)LiPh_3LiBr$ [15] and $(\overline{LiCHCH_2CH_2})(LiBr)_2$ [16]. For $[2,6\text{-}(2\text{-}MeOC_6H_4)_2C_6H_3LiTHF)LiI]_2$, a ladder

structure in which two LiI units form the central and two Li–C(*ipso*) form the terminal rings was observed. The structure of **3** is analogous to one half of this structure and the difference is due presumably to the chelating character of $[2,6\text{-}(2\text{-}MeOC_6H_4)_2C_6H_3LiTHF)LiI]_2$.

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Appendix A. Supplementary data

The X-ray data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-257182-257184. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam-ac.uk. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.01.011.

References

[1] (a) G.E. Coates, K. Wade, Organometallic Compounds, Methuen, London, 1967;
(b) B.J. Wakefield, The Chemistry of Organolithium Compounds, Pergamon Press, New York, 1974;
(c) Z. Rappoport, I. Marek, The Chemistry of Organolithium Compounds, Wiley, Chichester, 2004.
[2] (a) W.N. Setzer, R.v.R. Schleyer, Adv. Organomet. Chem. 24 (1985) 354;
(b) M.A. Beswick, D.S. WrightComprehensive Organometallic Chemistry II, vol. 2, Pergamon Press, New York, 1995, 1.
[3] (a) B. Twamley, P.P. Power, Adv. Organomet. Chem. 44 (1999) 1;
(b) J.A.C. Clyburne, N. McMullen, Coord. Chem. Rev. 210 (2000) 73.
[4] (a) S. Watanabe, K. Goto, T. Kawashima, R. Okazaki, Tetrahedron Lett. 36 (1995) 7677;
(b) U.L Luning, H. Baumgartner, Synlett 8 (1993) 571.
[5] (a) M.M. Olmstead, P.P. Power, J. Organomet. Chem. 408 (1991) 1;
(b) G.S. Girolami, M.E. Riehl, K.S. Suslick, S.R. Wilson, Organometallics 11 (1992) 3907.
[6] R.C. Crittendon, B.C. Beck, J. Su, X.W. Li, G.H. Robinson, Organometallics 18 (1999) 156.
[7] G.W. Rabe, R.D. Sommer, A.L. Rheingold, Organometallics 19 (2002) 5537.
[8] G.L. Wegner, R.J.F. Berger, A. Schier, H. Schmidbaur, Z. Naturforsch., B: Chem. Sci. 55 (2000) 995.
[9] N.J. Hardman, B. Twamley, M. Stender, R. Baldwin, S. Hino, B. Schiemenz, S. Kauzlarich, P.P. Power, J. Organomet. Chem. 643 (2002) 461.
[10] N.J. Hardman, R.J. Wright, A.D. Phillips, P.P. Power, J. Am. Chem. Soc. 123 (2003) 2667.
[11] B. Schiemenz, P.P. Power, Organometallics 15 (1996) 958.
[12] B. Schimenz, P.P. Power, Angew. Chem. Int. Ed. Engl. 35 (1996) 2150.
[13] K. Ruhlandt-Senge, J.J. Ellison, R.J. Wehmschulte, F. Pauer, P.P. Power, J. Am. Chem. Soc. 115 (1993) 11353.
[14] G.W. Rabe, M. Zhang-Presse, G.P.A. Yap, Acta Crystallogr., Sect. E: Struc. Rep. Online 58 (2002) m434.
[15] H. Hope, P.P. Power, J. Am. Chem. Soc. 105 (1983) 5320.
[16] H. Schmidbaur, A. Schier, U. Schubert, Chem. Ber. 116 (1983) 1938.
[17] P.D. Bartlett, M. Roha, R.M. Stiles, J. Am. Chem. Soc. 76 (1954) 2349.
[18] (a) A. Saednya, H. Hart, Synthesis (1996) 1455;
(b) R.S. Simons, S.T. Haubrich, B.V. Mork, M. Niemeyer, P.P. Power, Main Group Chem. 2 (1998) 275.
[19] H. Hope, in: A.L. Wayda, M.Y. Darensbourg (Eds.), Experimental Organometallic Chemistry, A Practicum in Synthesis and Characterization, ACS Symposium Series 357, American Chemical Society, Washington, DC, 1987 (Chapter 10).
[20] G.M. Sheldrick, SHELXTL-Plus, A Program Package for Refinement of Crystal Structures, Göttingen, 1989.
[21] SADABS and Empirical Absorption Correction Program Part of the SAINT Plus NT Version 50 Package, Bruker AXS, Madison, WI, 2003.
[22] M. Schlosser, V.J. Ladenberger, J. Organomet. Chem. 8 (1967) 193.
[23] D. Seebach, H. Neumann, Chem. Ber. 107 (1974) 847.