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Unusual structures of lithium terphenyl derivatives

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

The synthesis, spectroscopic and structural characterization of three new lithium derivatives of terphenyl ligands are reported. These are the mixed lithium alkyl–lithium aryl compound {Li(*t*-Bu)LiC_6H_3-2,6-$Trip_2$} (**1**, Trip = C_6H_2-2,4,6-*i*-Pr_3), the dilithiated {LiC_6H_3-2-(C_6H_3-2-Me-5-*t*-Bu)-6-(C_6H_3-2-CH_2Li-5-*t*-Bu)·Et_2O}$_2$ (**2**), and the ether solvated (Et_2O)LiC_6H_3-2,6-(C_6H_4-4-*t*-Bu)$_2$ (**3**). The synthesis of the terphenyl halide precursors for **2** and **3** is also given. The compound **1** resulted from the treatment of 1-IC_6H_3-2,6-Trip with two equivalents of Li(*t*-Bu) in hexane. It features the alkyl and aryl (terphenyl) groups bridged by two lithium ions. The lithium ions are further solvated by *ortho* aryl substituents and methyls of the *t*-Bu groups. This compound is a very rare example of a mixed lithium alkyl–lithium aryl species. Compound **2** was obtained in low yield from the treatment of 1-BrC_6H_3-2,6-(C_6H_3-2-Me-5-*t*-Bu)$_2$ with two equivalents of Li(*t*-Bu). The terphenyl ligand was dilithiated by replacement of the bromine and a hydrogen from one of the methyl groups on the *ortho* aryl substituents. The ether solvated, dimeric, tetrametallic structure illustrated in the Table of Contents resulted. The compound **3** was obtained from the straightforward lithiation of the iodoterphenyl precursor in the presence of diethyl ether and features a lithium ion solvated by two ethers terminally bound to the *ipso*-carbon of the terphenyl group. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Terphenyl; Lithium alkyl; Lithium aryl; C–H activation; Bulky groups

1. Introduction

The employment of *meta*-terphenyl ligands in the stabilization of compounds with unusual bonding has attracted considerable recent interest [1,2]. The lithium derivatives are the most important transfer agents for these ligands. Accordingly, knowledge of their structures and degree of aggregation are of importance in understanding their reactivity patterns. Since even the least crowded *meta*-terphenyl ligands are relatively bulky, the aggregation tendency of their lithium salts is low. At present only monomeric or dimeric structures are known. In the case of the monomers, the lithium is solvated by either one or two ethers or a benzene molecule as in (Et_2O)$_2$$LiC_6H_2$-2,4,6-$Ph_3$ [3,4], (Et_2O)$_2$$LiC_6H_3$-2,6-$Ph_2$ [5], (Et_2O)LiC_6H_3-2,6-$Trip_2$ (Trip = C_6H_2-2,4,6-*i*-Pr_3) [6] or (η^6-C_6H_6)LiC_6H_3-2,6-$Trip_2$ [7]. The dimeric structures are limited to two examples, which are both Lewis base free. Thus (LiC_6H_3-2,6-Mes_2)$_2$ (Mes = C_6H_2-2,4,6-Me_3) exists as a dimer with bridging σ-interactions involving Li–C(*ipso*) of the central aryl ring, as well as longer π-interactions involving the C(*ipso*) atoms of the *ortho* mesityl rings [8]. In contrast, the structure of (LiC_6H_3-2,6-$Dipp_2$)$_2$ (Dipp = C_6H_3-2,6-*i*-Pr_2) involves each lithium in a Li–C(*ipso*) σ-interaction to a central aryl ring, and dimerization is achieved by an η^6 π-interaction with one of the Dipp aryl substituents of the other terphenyl group of the dimer [7]. We now report two further examples of lithium terphenyl structural types that were previously unknown. These are the mixed lithium alkyl–lithium aryl species {Li(*t*-Bu)LiC_6H_3-2,6-$Trip_2$} (**1**), and the *ortho*-metallated, dilithium derivative {LiC_6H_3-2-(C_6H_3-2-Me-5-*t*-Bu)-6-(C_6H_3-2-CH_2Li-5-*t*-Bu)·Et_2O}$_2$ (**2**), in addition, we describe the structure of

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$(Et_2O)_2LiC_6H_3$-2,6(C_6H_4-4-*t*-Bu)$_2$ (**3**), which resembles those previously reported for $(Et_2O)_2LiC_6H_2$-2,4,6-Ph_3 [3,4] and $(Et_2O)_2LiC_6H_3$-2,6-Ph_2 [5].

2. Experimental

2.1. General procedures

All manipulations were carried out using modified Schlenk techniques under an atmosphere of N_2 or in a Vacuum Atmospheres HE-43 dry box. All solvents were distilled from Na–K alloy and degassed immediately before use. The compounds 1-IC_6H_3-2,6-$Trip_2$ [6,9] and 1-bromo-2-methyl-5-*t*-butylbenzene were synthesized as previously described. The compound 1-iodo-4-*t*-butylbenzene [10] and hexane or pentane solutions of Li(*n*-Bu), Li(*t*-Bu) were purchased commercially and used as received. ^{1}H-, ^{13}C- and ^{7}Li-NMR spectra were recorded on a Bruker 300 MHz instrument and referenced to the deuterated solvent.

2.2. *{Li(t-Bu)LiC$_6$H$_3$-2,6-Trip$_2$}* (*1*)

A 1.5 M pentane solution (20 ml, 30 mmol) of Li(*t*-Bu) was added dropwise to a slurry of 1-IC_6H_3-2,6-$Trip_2$ (8.44 g, 15 mmol) in hexane (100 ml) with cooling to ca. − 78 °C in a dry ice–acetone bath. The solution was allowed to come to room temperature (r.t.) over a period of 10 h, whereupon it was warmed to ca. 60 °C for 1 h. Cooling to r.t. followed by filtration through celite, afforded a pale yellow solution which was concentrated to ca. 60 ml under reduced pressure. Cooling in a ca. − 20 °C freezer afforded the product **1** as colorless crystals. Yield: 2.9 g, 36%. Melting point (m.p.): 180–181 °C. ^{1}H-NMR (300 MHz, C_6D_6): δ 0.71 (s, 9H, C(C*H*$_3$)$_3$), 1.14 (d, 12H, CH(C*H*$_3$)$_2$, $^3J_{HH} = 6.9$ Hz, 1.18 (d, 12H, CH(C*H*)), $^3J_{HH} = 6.9$ Hz, 1.19 (d, 12H, CH(C*H*$_3$)$_2$), $^3J_{HH} = 6.9$ Hz, 2.75 (sept, 2H, *p*-C*H*(CH$_3$)$_2$), $^3J_{HH} = 6.9$ Hz, 3.27 (sept, 4H, *o*-C*H*(CH$_3$)$_2$), $^3J_{HH} = 6.9$ Hz, 7.21 (s, 4H, *m*-Trip), 7.24 (t, 1H, *p*-C_6H_3), $^3J_{HH} = 6.9$ Hz, 7.29 (d, 2H, *m*-C_6H_3), $^3J_{HH} = 6.9$ Hz; ^{13}C{^{1}H}-NMR (75.44 MHz, C_6D_6): δ 10.46 (*C*(CH$_3$)$_3$), 23.75 (*o*-CHC(CH$_3$)$_2$), 24.24 (*p*-CH(*C*H$_3$), 24.78 (*o*-CH(*C*H$_3$), 30.38 (*o*-*C*H(CH$_3$)$_2$), 33.35 (C(*C*H$_3$)$_3$), 34.79 (*p*-*C*H(CH$_3$)$_2$), 122.55 (*m*-Trip), 123.78 (*m*-C_6H_3), 124.73 (*p*-C_6H_3), 142.04 (*i*-Trip), 147.43 (*o*-Trip), 148.76 (*p*-Trip), 149.55 (*m*-C_6H_3), 179.64 (*i*-C_6H_3); ^{7}Li-NMR (116.6 MHz, C_6D_6): δ 1.15.

2.3. *{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)·Et$_2$O}$_2$* (*2*)

1-Bromo-2-methyl-5-*t*-butylbenzene (45.43 g, 200 mmol) [10] in tetrahydrofuran (THF, 250 ml) was added dropwise to a rapidly stirred slurry of 4.86 g (200 mmol) of magnesium in THF (30 ml) to which had been added a few crystals of I_2. After the addition, the mixture was heated to ca. 60 °C to complete the reaction. Upon cooling, the Grignard solution was added dropwise to a well-stirred suspension formed by the addition of *n*-BuLi (65 ml, 104 mmol, in a 1.6 M hexane solution) to 1,3-dichlorobenzene (14.7 g, 100 mmol) in THF (20 ml) which was maintained at ca. − 70 °C with a dry ice–acetone cooling bath. When the addition was complete, the reaction mixture was allowed to come to r.t. (3 h) and heated to reflux for 1 h. The mixture was then cooled to ca. − 10 °C with an ice–salt mixture and treated dropwise with Br_2 (22.4 g, 140 mmol). Upon warming to r.t., the mixture was hydrolyzed with aqueous (aq.) HCl (300 ml, 0.1 M). The phases were separated and the aq. phase was extracted with methybutyl ether (2 × 50 ml). The combined organic phase were decolorized (red–orange to yellow) and concentrated on a rotary evaporator to give an amber oil (49.3 g). The oil was purified by fractional distillation (230 °C, 3 mmHg) to afford the product 1-BrC_6H_3-2,6(C_6H_3-2-Me-5-*t*-Bu)$_2$ (IUPAC name: 2′-bromo-5,5-di-*t*-butyl-2,2″-dimethyl-[1,1′; 3″,1″ terphenyl) as a pale yellow, glassy solid. Yield: 35.1 g, 78%. M.p.: 54–56 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.38 (br s, 18H, C(C*H*$_3$)$_3$), 2.15 (br s, 6H, CH$_3$), 7.25 (br m, Ar–H), 7.36 (br m, Ar–H). ^{1}H-NMR (300 MHz, C_6D_6): δ 1.23 (s, 18H, C(CH$_3$)$_3$), 2.20 (2, 6H, CH$_3$), 7.08 (m, Ar–H), 7.16 (m, Ar–H), 7.26 (d, Ar–H), 7.29 (d, Ar–H), 7.37 (d, Ar–H), 7.41 (br s, Ar–H). ^{13}C{^{1}H}-NMR (75.44 MHz, $CDCl_3$): δ 19.34, 19.60, 31.51, 34.51, 122.30, 124.49, 126.16, 126.50, 126.72, 129.19, 129.25, 129.41, 132.65, 132.77, 141.28, 143.66, 148.12, 148.23.

An ether–hexane solution (30 ml, 1:5) of the brominated terphenyl (1.0 g, 2.22 mmol) was cooled to ca. − 78 °C in a dry ice–acetone bath and treated dropwise with Li(*t*-Bu) (2.76 ml of a 1.6 M solution, 4.42 mmol). The solution became orange and deposited a pale yellow precipitate and was stirred for a further 1 h. Stirring was continued overnight at r.t. and the solvent was removed under reduced pressure. The resulting solid was extracted with pentane (40 ml) and the solid allowed to settle. The supernatant solution was filtered and concentrated to ca. 15 ml. Cooling in a − 20 °C freezer for 2 days afforded the product **2** as orange–yellow crystals. Yield: 0.04 g, 4%. M.p. (dec.) > 100 °C. ^{1}H-NMR (300 MHz, C_6D_6): δ 0.29 (br s, 2H, LiC*H*$_2$), 0.52 (t, 6H, C*H*$_3$CH$_2$O), 1.35 (br s, 18H, C(CH$_3$)$_3$), 2.33 (br s, 6H, Me), 2.84 (q, 4H, OC*H*$_2$CH$_3$), 7.31 (m, br, 9H, Ar–H).

2.4. *(Et$_2$O)$_2$LiC$_6$H$_3$-2,6(C$_6$H$_4$-4-t-Bu)$_2$* (*3*)

A THF (200 ml) solution of 1,3-dichlorobenzene (8.0 g, 54.4 mmol) was treated dropwise over a period of ca.

1 h with Li(*n*-Bu) (34 ml of a 1.6 M solution in hexane) with rapid stirring and cooling to ca. −78 °C in a dry ice bath. The resulting white suspension was stirred for a further 1.5 h. A solution of 1-BrMgC_6H_4-4-*t*-Bu (synthesized in THF (100 ml) by the reaction of 1-Br-4-*t*-BuC_6H_4 (30 g, 142 mmol) with magnesium turning (3.5 g, 144 mmol)) was added dropwise while maintaining the low temperature (ca. −78 °C) with a dry ice–acetone bath. After 1 h, the solution was allowed to come to r.t. and refluxed for 1 h. Upon cooling to r.t., the solution was treated with I_2 (30 g, 117 mmol) and stirred for 1 h. The solution was treated with an aq. sodium sulfate solution (200 ml). The layers were separated and the aq. layer was washed with ether (2 × 50 ml). The combined organic layer was dried with magnesium sulfate and the ether was removed under reduced pressure. The resulting yellow solid was recrystallized from hot ethanol (EtOH). The product was sublimed under reduced pressure (0.01 mmHg) at 15 °C to afford 1-IC_6H_3-2,6-(C_6H_4-4-*t*-Bu)$_2$ as colorless crystals. Yield: 21.6 g, 85%. M.p.: 179–182 °C. ^{1}H-NMR (400 MHz, C_6D_6): δ 1.13 (s, 18H, C(CH_3)$_3$), 6.98 (t, 1H, *p*-C_6H_3), 7.08 (d, 2H, *m*-C_6H_3), 7.28 (q, 8H, *o*- and *m*-C_6H_4). ^{13}C{^{1}H}-NMR (100.5 MHz; C_6D_6): δ 31.4 (C(CH_3)), 34.5 (*C*(CH_3)), 104.7 (I–*C*), 125.1, 127.8, 129.0, 129.5 (Ar–C).

The iodoterphenyl (5 g, 10.65 mmol) in hexane (20 ml) in a dry ice–acetone bath was treated dropwise with Li(*n*-Bu) (6.7 ml of a 1.6 M solution in hexane) with rapid stirring. The solution was allowed to come to r.t. and stirred for a further 1 h. The solvent was pumped off and the residue was taken up in hexane (50 ml). Filtration followed by the addition of Et_2O (10 ml), reduction in volume to ca. 15 ml and cooling in a ca. −20 °C freezer gave the product **3** as colorless crystals. Yield: 2.2 g, 42%. M.p. (dec.): 114–117 °C. ^{1}H (400 MHz, C_6D_6): δ 0.25 (t, 12H, OCH_2CH_3), $^3J_{HH} =$ 7.5 Hz, 1.37 (s, 18H, C(CH_3)$_3$), 2.63 (q, 8H, OC$H_2$$CH_3$), $^3J_{HH} = 7.5$ Hz, 7.28 (br m, 3H, C_6H_3), 7.38 (q, 8H, C_6H_4). ^{13}C{^{1}H}-NMR (100.5 MHz, C_6D_6): δ 14.5 (OCH*C*H_3), 31.4 (C(*C*H_3)$_3$), 34.6 (*C*(CH_3)$_3$), 68.2 (O*C*$H_2$$CH_3$), 124.7, 127.5, 128.6, 129.0, 142.7, 148.0, 150.3 (Ar–C), 175.3 (*i*-C_6H_3).

2.5. 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 [11]. All data were obtained using a Bruker SMART 1000 diffractometer and Mo–K_α radiation. The SHELXTL version 5.03 program package was used for the structure solutions and refinements [12]. Absorption corrections were applied using the SADABS program [13]. The structures were solved by direct methods and refined by full matrix least-squares procedures. All non-hydrogen atoms were refined aniostropically. Hydrogen atoms 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** and **2** were obtained by the reaction of Li(*t*-Bu) with the corresponding terphenyl halide derivatives. The halide precursors were synthesized by modifications [9,14] of the original route of Hart and coworkers [15]. The precursors to **1** and **3** were colorless crystalline solids whereas that for **2** had the appearance of a glass that softened (melted) at 54–56 °C. The use of this reaction to obtain lithium terphenyl compounds was first reported in 1991 [3,4] and remains the preferred route for these compounds. Originally, this reaction involved the use of one equivalent of lithium alkyl with the terphenyl halide as shown by reaction (1).

$$\text{Li}(n\text{-Bu}) + 1\text{-IC}_6\text{H}_2\text{-2,4,6-Ph}_3 \rightarrow \text{LiC}_6\text{H}_2\text{-2,4,6-Ph}_3 + n\text{-BuI} \qquad (1)$$

Subsequent experiments have shown that the use of two equivalents of the lithium alkyl afforded higher yields of the lithium terphenyls as exemplified in reaction (2).

$$1\text{-IC}_6\text{H}_3\text{-2,6-Trip}_2 + 2\text{Li}(t\text{-Bu}) \xrightarrow{\text{Et}_2\text{O}} (\text{Et}_2\text{O})\text{LiC}_6\text{H}_3\text{-2,6-Trip}_2 + \text{LiI} + \text{C}_4\text{H}_{10} + \text{C}_4\text{H}_8 \qquad (2)$$

In effect, the second equivalent of lithium alkyl displaces the equilibrium to the right so that the reaction proceeds further toward completion. For the very crowding terphenyl group –C_6H_3-2,6-Trip$_2$ monomeric salts (Et_2O)LiC_6H_3-2,6-Trip$_2$ or (η^6-C_6H_6)LiC_6H_3-2,6-Trip$_2$ are obtained [6,7] when the reaction is carried out in the presence of diethyl ether or benzene. If the ether or benzene is omitted and the reaction is performed in hexane the product **1** is obtained.

$$1\text{-IC}_6\text{H}_3\text{-2,6-Trip}_2 + 2\text{Li}(t\text{-Bu}) \rightarrow \text{Li}(t\text{-Bu}) \; \text{LiC}_6\text{H}_3\text{-2,6-Trip}_2\, \mathbf{1} + \text{LiI} + 1/2\text{C}_6\text{H}_{10} + 1/2\text{C}_4\text{H}_8 \qquad (3)$$

Presumably ether complexation of the lithium aryl, as in reaction (2), prevents formation of the lithium alkyl–

lithium aryl as seen in reaction (3). Compound **1** is a rare example of a mixed organolithium derivative, i.e. a molecular organolithium species in which there are two or more different organic anions. Structurally characterized examples include $\{Li(n\text{-}Bu)LiMes^*\}_2$ ($Mes^* = C_6H_2\text{-}2,4,6\text{-}t\text{-}Bu_3$) [8] and $\{Li(n\text{-}Bu)CH_2C_6H_3\text{-}2,6(CH_2NMe_2)_2\text{-}3,5\text{-}Me_2\}_2$ [16].

The unusual, dilithiated compound **2** was obtained by the addition of two equivalents of Li(*t*-Bu) to the iodide. The product **2** is obtained in relatively low yield. The major co-product has ^{1}H- and ^{13}C-NMR spectra that are consistent with a species that is monolithiated at the *ipso*-carbon of the central aromatic ring. Unfortunately, no crystals of this compound suitable for X-ray crystallography have been obtained to date. Although the compound appears to be the first activation of a C–H bond on an *ortho* substituent of a terphenyl ligand by an organolithium reagent, there have been previous C–H activations of the $–C_6H_3\text{-}2,6\text{-}Mes_2$ or $–C_6H_3\text{-}Trip_2$ terphenyl ligands during the course of reduction of their derivatives of boron [17,18] or phosphorus halides [19]. The reasons for the activation of one of the methyl groups of the $–C_6H_3\text{-}2,6(C_6H_3\text{-}2,Me\text{-}5\text{-}t\text{-}Bu)_2$ group are not known with certainty. Possibly, the unique configuration of the molecule induced by the relative positions of the *t*-Bu and Me substituents may facilitate the deprotonation of the methyl moiety.

The compound **3** was obtained in moderate yield by the 1:1 reaction of Li–*n*-Bu with the iodoterphenyl precursor. This method was very similar to that originally used for the synthesis of the etherate $(Et_2O)_2LiC_6H_2\text{-}2,4,6\text{-}Ph_3$ [3,4].

3.2. Structures

The structure of **1** is illustrated in Fig. 1. The molecules consist of associated Li(*t*-Bu) and $LiC_6H_3\text{-}2,6\text{-}Trip_2$ units in which two lithiums bridge the $C_6H_3\text{-}2,6\text{-}Trip_2$ and *t*-Bu groups. There is no crystallographically required symmetry. The lithiums interact primarily with the *ipso*-carbon (C(1)) of the central aryl ring and the quaternary carbon (C(37)) of the *t*-Bu group. The Li–C(1) distances (av. 2.169(5) Å) are slightly longer than those between the lithiums and C(37) (av. 2.104(6) Å). The Li–C bonds in **1** are significantly, ca. 0.1–0.15 Å, shorter than those observed in the dimer $\{LiC(SiMe_3)_3\}_2$ [20] which features Li–C = ca. 2.30 Å. It seems probable that the large steric bulk of the $–C(SiMe_3)_3$ group causes the lengthening of the bonds. However, the Li–C(1) distances in **1** are similar

Table 1
Crystallographic data of compounds **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{40}H_{58}Li_2$	$C_{64}H_{84}Li_4O_2$	$C_{34}H_{49}LiO_2$
Formula weight	552.74	913.08	496.67
Color	Colorless	Orange	Colorless
Crystal dimensions (mm)	0.40 × 0.18 × 0.16	0.26 × 0.13 × 0.07	0.41 × 0.30 × 0.18
Crystal habit	Block	Parallelepiped	Plate
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	8.7515(5)	22.410(2)	10.952(2)
b (Å)	13.2181(7)	15.549(1)	12.078(2)
c (Å)	17.2513(9)	17.058(1)	13.239(3)
α (°)	109.172(1)		92.847(4)
β (°)	91.191(1)	90.037(2)	98.276(4)
γ (°)	107.443(1)		116.315(3)
V (Å^3)	1782.4(2)	5994.0(8)	1540.6(5)
Z	2	4	2
D_{calc} (g cm^{-3})	1.030	1.020	1.071
Absorption coefficient (mm^{-1})	0.056	0.058	0.063
F(000)	608	1984	544
Radiation λ (Å)	0.71073	0.71073	0.71073
Temperature (K)	93	93	90
2θ (°)	58	50	62.9
Unique data	9419	5232	9182
Observed data ($I > 2\sigma(I)$)	4554	2797	5767
R_{int}	0.0779	0.1026	0.0477
Parameters	427	322	339
R_1 ($I > 2\sigma(I)$)	0.0557	0.0535	0.0982
wR_2 (all data)	0.1401	0.1170	0.2759

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

1		**2**		**3**	
Bond lengths					
Li(1)–C(1)	2.168(4)	Li(1)–C(1)	2.139(5)	Li(1)–C(1)	2.110(6)
Li(2)–C(1)	2.170(5)	Li(2)–C(1)	2.127(4)	Li(1)–O(1)	1.952(5)
Li(1)–C(37)	2.110(4)	Li(1)–C(19A)	2.286(4)	Li(1)–O(2)	1.949(5)
Li(2)–C(37)	2.097(4)	Li(2)–C(19)	2.190(5)	C(1)–C(2)	1.414(4)
Li(1)···C(2)	2.636(4)	Li(2)···C(18A)	2.278(4)	C(1)–C(6)	1.423(4)
Li(1)···C(13)	2.299(4)	Li(2)···C(17A)	2.354(5)		
Li(1)···C(14)	2.721(4)	Li(2)···C(19A)	2.337(5)		
Li(1)···C(18)	2.631(4)	Li(1)···C(2)	2.695(5)		
Li(1)···C(38)	2.369(4)	Li(1)···C(13)	2.723(5)		
Li(2)···C(6)	2.621(4)	Li(1)–O(1)	1.911(5)		
Li(2)···C(7)	2.296(4)	C(1)–C(2)	1.419(3)		
Li(2)···C(8)	2.729(4)	C(2)–C(6)	1.420(3)		
Li(2)···C(12)	2.651(4)	C(18)–C(19)	1.474(3)		
Li(1)···Li(2)	2.225(5)	C(8)–C(28)	1.507(3)		
C(1)–C(2)	1.415(2)				
C(1)–C(6)	1.420(2)				
Bond angles					
Li(1)–C(1)–Li(2)	61.7(1)	Li(1)–(C1)–C(2)	71.0(2)	C(1)–Li(1)–O(2)	116.7(3)
Li(1)–C(1)–C(2)	92.3(1)	Li(2)–C(19A)–Li(2)	64.8(2)	C(1)–Li(1)–O(1)	118.5(3)
Li(2)–C(1)–C(6)	91.3(1)	C(1)–Li(1)–C(19A)	111.8(2)	C(1)–Li(2)–O(2)	124.8(3)
C(2)–C(37)–Li(2)	114.7(2)	C(1)–Li(2)–C(19A)	110.3(2)	C(2)–C(1)–C(6)	114.1(2)
Li(1)–C(37)–Li(2)	63.9(2)	C(1)–C(2)–C(13)	118.6(2)	C(1)–C(2)–C(13)	120.0(2)
C(1)–Li(1)–C(37)	117.0(2)	C(1)–C(6)–C(7)	118.2(2)	C(1)–C(6)–C(7)	119.9(2)
C(1)–Li(2)–C(37)	117.5(2)	C(2)–C(1)–C(8)	115.1(2)		
C(2)–C(1)–C(6)	114.7(2)				
C(1)–C(2)vC(13)	115.2(2)				
C(1)–C(6)–C(7)	116.4(2)				
C(38)–C(37)–C(39)	107.4(2)				
C(38)–C(37)–C(40)	107.9(2)				
C(39)–C(37)–C(40)	107.7(2)				

to the average value of 2.165(10) Å observed in the structure of the dimer $(LiC_6H_3\text{-}2,6\text{-}Mes_2)_2$ [8] which involves two bridging lithiums bound primarily to two *ipso*-carbons. The Li–C(1)–Li angles 61.7(1)° (**1**) and 63.2(5) Å are also very similar in the two molecules. The coordination environment at C(1) is essentially planar and its carbanionic character is manifested in relatively narrow ring C(2)–C(1)–C(6) angle of 114.7(2)° at the *ipso* carbon. The carbanionic character of C(37) of the *t*-Bu group is manifested in C–C–C angles in the range 107.4(2)–107.9(2) which are ca. 2° less than idealized tetrahedral values. The core array C(1)–Li(1)–Li(2)–C(37) is also close to planarity and has an overall diamond shape, since the Li(1)–C(37)–Li(2) angle of 63.9(1)° is close to the corresponding angle at C(1) and the two C–Li–C angles within the core are very similar. Relatively close interactions are observed between the lithiums and other carbons or C–H groups within the molecule. Thus Li(1) interacts significantly with C(13) (2.299(4) Å) and C(38) from the *t*-Bu group (2.369(4) Å). Similar interactions are observed for Li(2) with C(7) and C(40) (cf. Table 2). The Li···Li separation in **1**, 2.225(5) Å is relatively short but similar to the 2.27(2) Å in $\{LiC_6H_3\text{-}2,6\text{-}Mes_2\}_2$ [8].

In summary, the overall structure of **1** presents a picture of a relatively strongly associated organolithium species in which the Li–C bonds are at the shorter end of the Li–C bond scale. The protected wedge shaped space and solvation afforded by the flanking Trip substituents probably contributes significantly to the stability of the aggregate. This assertion is supported by the fact that C(1)–C(2)–C(13) and C(1)–C(6)–C(7) angles involving the Trip substituents are less than 120° (cf. Table 2) which suggests an attractive interaction between the lithiums and the *ipso* carbons (i.e. C(7) and

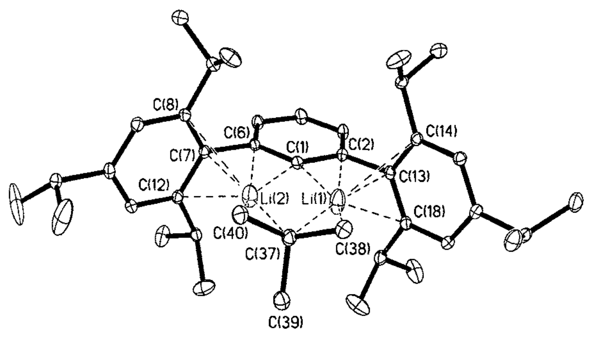

Fig. 1. Thermal ellipsoid plot (30%) of **1**.

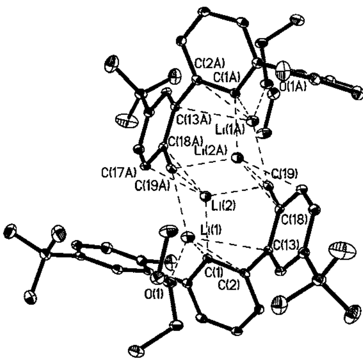

Fig. 2. Thermal ellipsoid plot (30%) of **2**.

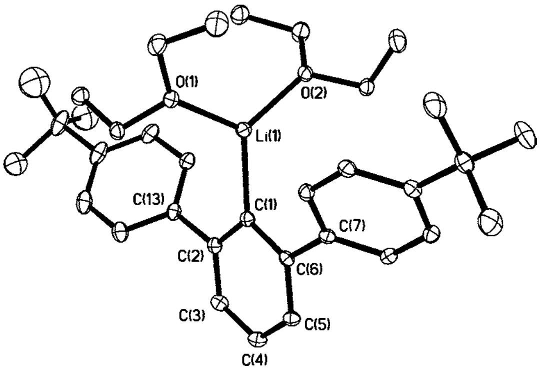

Fig. 3. Thermal ellipsoid plot (30%) of **3**.

C(13)) of the Trip substituents. It may be noted that these angles are slightly less than the corresponding angles (119.2(2) and 118.0(2)°) observed in $(Et_2O)LiC_6H_3$-2,6-$Trip_2$ which has the same terphenyl ligand but only one lithium in the wedge.

The structure of **2** is illustrated in Fig. 2. The dilithiated terphenyl ligands are associated through lithium bridging to afford a centrosymmetric dimeric structure. However, the bridging differs from that seen in **1**. The 'outer' lithiums i.e. Li(1) and Li(1A), which are each solvated by an ether, bridge the *ipso*-carbon (C(1)) of the central aryl ligand ring and a deprotonated methyl group (C(19A)) of the other terphenyl ligand in the dimer. The 'inner' lithiums Li(2) and Li(2A), which do not carry ether, also bridge C(1) and C(19A), and are further associated with a deprotonated methyl group (C(19)) within the same asymmetric unit. These Li–C interactions fall in the range 2.127(4)–2.286(4) Å. There are also relatively close interactions between Li(2) and C(17) and C(18) adjacent to the deprotonated carbon C(19). However, possible interactions between Li(1) and C(2) or C(13) are ca. 2.7 Å and are liable to be very weak and essentially negligible. To a first approximation Li(1) (and Li(1A)) is three coordinate and this is reflected in a relatively short distance to C(1) and a slightly longer interaction with C(19A). The Li–O bond length of 1.911(5) Å is also consistent with three coordinate lithium and is very similar to the 1.930(3) Å observed in the structure of $\{(Et_2O)LiTrip\}_2$ [21] which has a very similar lithium coordination environment. The Li(2) can be regarded as a pseudo three coordinate since it bridges C(19) and C(19A), as well as C(1). The bridging of C(19) and C(19A) is not symmetric, however, since these Li(2)–C(19)/C(19A) distance differ by ca. 0.15 Å. This difference is connected with the further close contacts between Li(2) and C(17A) and C(18A) (2.354(4) and 2.278(4) Å). In effect, Li(2) bridges C(1), C(19) and a three carbon C(19A), C(17A) and C(18A) unit. The C(18)–C(19) distance, 1.474(3) Å, associated with the deprotonated methyl group is shorter than the corresponding C(8)–C(28) distance for the undeprotonated methyl group 1.507(3) Å. This suggests multiple character in the C(18)–C(19) bond and some delocalization of the negative charge which is consistent with the interaction between Li(2) and C(18A). However, the C(18)–C(13) and C(18)–C(17) distances within the aryl ring do not display any unusual bond lengths. As in the case of **1**, the anionic character of the C(1) atom is reflected in a narrower C(2)–C(1)–C(6) angle of 115.1(2)°. The C(1)–C(2)–C(13) and C(1)–C(6)–C(7) angles are also less than the idealized 120°, possibly as a result of the attractive forces between the lithium ions and the π-electron density of the *ortho* aryl substituents.

The structure of **3** is illustrated in Fig. 3. It is a monomeric species with the lithium bound to an *ipso*-carbon in a terminal fashion. The lithium ion is also bound to two ethers to afford a three-coordinate planar environment at the metal. The Li–C distance, 2.1110(6) Å, is very similar to the shorter Li–C distances seen in **1** and **2** and to those reported previously for the compounds $(Et_2O)_2LiC_6H_2$-2,4,6-Ph_3 (2.07(2), 2.08(2) Å) [3,4] and $(Et_2O)_2LiC_6H_3$-2,6-Ph_2 (2.106(9) Å) [5]. The Li–O distances, av. 1.951(5) Å, are also the same as those previously observed in the latter species 1.94(2)–1.97(2) Å. The O–Li–O angle, 116.7(3)°, is similar to the 118.4(4) observed in $(Et_2O)_2LiC_6H_3$-2,6-Ph_3. The angle at *ipso*-carbon bearing the negative charge is 114.1(2)° which is slightly narrower by ca. 2° than those observed in $(Et_2O)_2LiC_6H_2$-2,4,6-Ph_3. The external angles at the *ortho*-carbons of the central ring C(1)–C(2)–C(13) and C(1)–C(6)–C(7) are very close to 120° and show no sign of being attracted to the positive charge at lithium. In essence, the presence of the *para* *t*-Bu substituent produces little change in the lithium carbon bonding.

4. Supplementary material

The X-ray data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-169221-169223. 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).

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References

[1] B. Twamley, S.T. Haubrich, P.P. Power, Adv. Organomet. Chem. 44 (1999) 1.
[2] J.A.C. Clyburne, N. McMullen, Coord. Chem. Rev. 210 (2000) 73.
[3] M.M. Olmstead, P.P. Power, J. Organomet. Chem. 408 (1991) 1.
[4] G.S. Girolami, M.E. Riehl, K.S. Suslick, S.R. Wilson, Organometallics 11 (1992) 3907.
[5] R.C. Crittendon, B.C. Beck, J. Su, X.-W. Li, G.H. Robinson, Organometallics 18 (1999) 156.
[6] B. Schiemenz, P.P. Power, Organometallics 15 (1996) 958.
[7] B. Schiemenz, P.P. Power, Angew. Chem. Int. Ed. 35 (1996) 2150.
[8] K. Ruhlandt-Senge, J.J. Ellison, R.J. Wehmschulte, F. Pauer, P.P. Power, J. Am. Chem. Soc. 115 (1993) 11353.
[9] R.S. Simons, S.T. Haubrich, B.V. Mork, M. Niemeyer, P.P. Power, Main Gp. Chem. 2 (1998) 275.
[10] L.M. Stock, H.C. Brown, J. Am. Chem. Soc. 51 (1959) 5615.
[11] H. Hope, in: A.L. Wayda, M.Y. Darensbourg (Eds.), Experimental Organometallic Chemistry. A Practicum in Synthesis and Characterization, American Chemical Society, Washington, DC, 1987 Chapter 10, ACS Sym. Ser. 357.
[12] G.M. Sheldrick. SHELXTL-Plus. A program package for refinement of crystal structures, Göttingen, 1989.
[13] SADABS an empirical absorption correction program part of the SAINT Plus NT version 50 package; Bruker AXS: Madison, WI, 1998.
[14] C.-J. Du, H. Hart, D.K.-K. Ng, J. Org. Chem. 51 (1986) 3162.
[15] A. Saednya, H. Hart. Synthesis (1996) 1455.
[16] P. Wijkens, E.M. van Kolen, M.D. Janssen, J.T.B.H. Jastrzebski, A.L. Spek, G. van Koten, Angew. Chem. Int. Ed. 34 (1995) 219.
[17] W.J. Grigsby, P.P. Power, J. Am. Chem. Soc. 118 (1996) 7981.
[18] R.J. Wehmschulte, M.A. Khan, B. Twamley, B. Schiemenz, Organometallics 20 (2000) 844.
[19] B. Twamley, C.D. Sofield, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 121 (1999) 3357.
[20] W. Hiller, M. Layh, W. Uhl, Angew. Chem. Int. Ed. Engl. 30 (1991) 324.
[21] R.A. Bartlett, H.V.R. Dias, P.P. Power, J. Organomet. Chem. 341 (1988) 1.