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Isolation and X-ray crystal structure of a monomeric, σ -bonded aryllithium etherate complex [Li(Et₂O)₂-2,4,6-Ph₃C₆H₂]

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Abstract

The organolithium etherate complex [Li(Et₂O)₂-2,4,6-Ph₃C₆H₂], **1**, has been crystallized from an ether/hexane solution, and characterized by ¹H NMR and X-ray crystallography. The complex **1** has the rare mononuclear structure, and it is the first instance of a monomeric aryllithium etherate crystal structure in which the Li⁺ ion interacts in σ -fashion to the organic moiety. The Li⁺ ion, which is solvated by two ethers, has trigonal planar coordination and the Li–C distance is 2.074(16) Å. Although **1** is a sterically crowded molecule its structural features display little evidence of steric strain.

Introduction

In this laboratory, work on the structures of organolithium compounds and related species has been focussed on the crystallization of ether (OR₂) solvated complexes [1–3]. This is because organolithium reagents are, most often, used in these solvents. Thus, the structural data obtained in the solid state may provide a fairly accurate picture of what the structure could be in the solution phase. Currently, the structures of about twelve ether solvated complexes are known [1–8] and, with the exception of two delocalized complexes [3,7], and the species [Li(THF)C(SiMe₂Ph)₃] [6] (which has an interaction between Li⁺ and one of the phenyl rings), and the ionic compound [Li(THF)₄][Li{C(SiMe₃)₃}₂] [5], they are associated in the crystal phase. Recent work on aryllithium etherate complexes has shown that the degree of association can be reduced by using larger substituents [2,3]. Thus, phenyllithium may be crystallized as the tetramer [(PhLi·Et₂O)₄] [1] whereas mesityllithium crystallizes as the dimer [{Li(THF)₂Mes}₂] [2]. In addition, Li(2,4,6-*i*-Pr₃C₆H₂) (LiTrip) crystallizes as the dimer [{Li(Et₂O)Trip}₂] [3]. Moreover, in this complex, the coordination number at Li⁺ has been reduced to three and the bridging Li–C bonds become asymmetric (2.249(3) and 2.203(3) Å). This suggests that a marginal increase in the size of the *ortho*-substituents should give a monomeric complex. Although Li(2,4,6-*t*-Bu₃C₆H₂) (abbreviated LiMes^{*}) yielded crystals from an ether/hexane solution, the crystals were not suitable for X-ray crystallography. It has been shown by others that the addition of TMEDA to

LiMes^{*}, however, did give a monomeric complex, which has been structurally characterized [9]. In order to obtain crystals of a monomeric σ -bonded etherate complex we turned to the readily available ligand 2,4,6-Ph₃C₆H₂ (Triph), which had been found to be effective in the steric protection of porphyrins [10]. In addition, use of the Triph group had allowed the unique monomeric derivatives MTriph (M = Cu or Ag) to be crystallized and structurally characterized [11]. In this paper the facile synthesis and X-ray crystal structure of the bis(diethyletherate)Li⁺ salt of this ligand is described [12*].

Experimental

All operations were performed under an N₂ atmosphere by using modified Schlenk techniques. The solvents were distilled from conventional drying agents and degassed twice prior to use. 1,3,5-Ph₃C₆H₃ was used as purchased and TriphBr was synthesized by a slightly modified literature procedure [13].

Synthesis of 1

[Li(Et₂O)₂Triph] (**1**). TriphBr (7.7 g, 20 mmol) in Et₂O (30 mL) and hexane (5 mL) was cooled in an ice bath. With vigorous stirring, BuLi in hexane (1.6 M; 12.5 mL) was added dropwise. The solution, which was initially colorless, became yellow during the addition. The ice bath was then removed and the solution was stirred for a further 2 h. The solvent was removed under reduced pressure until a precipitate appeared. The solution was then warmed to redissolve the pale yellow precipitate. Overnight cooling in a -20°C freezer gave the product **1** as pale yellow crystals. Yield 87% (8.2 g), m.p. 72–74°C; ¹H NMR (C₆D₆), 300 K: 7.75 (s (2H), *m*-H), 7.66 (d), 7.44 (d), 7.3 (t), 7.27 (t), 7.176 (t), 3.0 (q, CH₂) 0.8 (t, CH₃).

X-Ray crystallographic studies

All data were collected with a Syntex P2₁ diffractometer equipped with a locally modified LT-1 low temperature device using Mo-K_α radiation ($\lambda = 0.71069 \text{ \AA}$). Calculations were carried out on a Data General Eclipse computer using SHELXTL programs versions 4 and 5. The atomic form factors including anomalous dispersion scattering were from Ref. 14. Colorless plates of **1** were obtained as described above. To prevent possible reaction with the air or loss of solvent, the crystals were left in the mother liquor until ready for use. A sample was removed under an N₂ flow and covered with a hydrocarbon oil from which a single crystal was selected, attached to a glass fiber on a mounting pin with silicon grease and immediately placed on the diffractometer in a low temperature N₂ stream (130 K). Crystal data are as follows: **1**, C₃₂H₃₇LiO₂, fw = 460.59, $a = 12.012(2) \text{ \AA}$, $b = 19.631(3) \text{ \AA}$, $c = 22.948(4) \text{ \AA}$, orthorhombic, space group *Pcab* (*bac* of *Pbca*, No. 61) [15*] $Z = 8$, $V = 5411(2) \text{ \AA}^3$, $d_{\text{calc}} = 1.13 \text{ g cm}^{-3}$, 1176 unique observed data ($I > 3\sigma(I)$), $R = 0.072$, $R_w = 0.059$. Further details are provided in the supplementary material. The atom coordinates are listed in Table 1. Selected bond distances and angles are provided in Table 2. Complete tables of bond distances, angles and hydrogen coordinates are also provided in the supplementary material.

* Reference number with asterisk indicates a note in the list of references.

Table 1

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $[\text{Li}(\text{Et}_2\text{O})_2\text{Triph}]$, **1**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ^a
O(1)	3568(5)	6758(3)	4161(3)	28(2)
O(2)	5794(5)	6806(4)	3355(3)	40(2)
C(1)	4825(7)	5169(4)	3774(4)	18(2)
C(2)	3993(7)	4760(5)	3510(4)	18(3)
C(3)	3972(7)	4046(5)	3513(4)	19(3)
C(4)	4838(0)	3678(4)	3780(5)	17(2)
C(5)	5701(7)	4055(5)	4016(4)	18(2)
C(6)	5694(7)	4765(4)	4022(4)	21(2)
C(7)	3061(7)	5107(5)	3190(4)	18(3)
C(8)	3285(7)	5600(5)	2760(4)	22(3)
C(9)	2440(7)	5900(5)	2453(4)	32(3)
C(10)	1336(8)	5749(5)	2568(4)	34(3)
C(11)	1094(7)	5268(5)	2997(4)	30(3)
C(12)	1944(8)	4951(5)	3315(4)	27(3)
C(13)	4833(7)	2925(4)	3775(4)	16(2)
C(14)	3848(7)	2551(5)	3877(3)	24(3)
C(15)	3860(7)	1854(4)	3890(3)	24(3)
C(16)	4838(8)	1490(4)	3795(4)	25(2)
C(17)	5823(8)	1844(4)	3698(4)	22(2)
C(18)	5805(7)	2566(5)	3692(4)	17(2)
C(19)	6660(6)	5116(4)	4313(4)	11(2)
C(20)	7743(7)	4997(5)	4157(4)	17(2)
C(21)	8644(8)	5306(5)	4412(4)	26(3)
C(22)	8444(8)	5770(5)	4865(4)	33(3)
C(23)	7360(7)	5904(5)	5033(4)	25(3)
C(24)	6462(8)	5579(5)	4770(4)	26(3)
C(25)	2029(8)	6053(6)	4531(4)	37(3)
C(26)	2419(8)	6554(4)	4082(4)	34(3)
C(27)	3704(8)	7239(5)	4627(4)	39(3)
C(28)	4898(8)	7460(6)	4661(4)	50(3)
C(29)	4514(9)	7523(7)	2853(5)	74(4)
C(30)	5636(10)	72,46(6)	2892(5)	78(4)
C(31)	6969(8)	6609(6)	3427(4)	50(3)
C(32)	7302(9)	6110(6)	2963(5)	56(4)
Li	4722(14)	6224(7)	3773(8)	30(4)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 2

Selected bond distances (\AA) and angles ($^\circ$) for **1**

Li–C(1)	2.074(16)	C(5)–C(6)	1.395(12)
Li–O(1)	1.954(18)	C(6)–C(1)	1.429(12)
Li–O(2)	1.971(18)	C(2)–C(7)	1.502(13)
C(1)–C(2)	1.418(12)	C(4)–C(13)	1.479(10)
C(2)–C(3)	1.401(13)	C(6)–C(19)	1.506(12)
C(3)–C(4)	1.407(12)		
C(4)–C(5)	1.383(13)		
O(1)–Li–O(2)	111.9(7)	C(4)–C(5)–C(6)	122.3(8)
O(1)–Li–C(1)	125.3(9)	C(5)–C(6)–C(1)	123.7(8)
O(2)–Li–C(1)	122.8(9)	C(1)–C(2)–C(7)	118.4(8)
C(2)–C(1)–C(6)	111.7(7)	C(1)–C(6)–C(19)	119.1(7)
C(1)–C(2)–C(3)	125.3(8)		
C(2)–C(3)–C(4)	120.1(8)		
C(3)–C(4)–C(5)	116.7(7)		

The orientation matrix and cell dimension were obtained by a least-squares fit of 24 well-centered reflections with $20^\circ < 2\theta < 30^\circ$. The structure was solved by direct methods. Hydrogen atoms were included using a riding model with $r(\text{C-H})$ of 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{iso}}(\text{C})$. The structure was not refined anisotropically due to the low number of observed reflections (1176 with $I > 3\sigma(I)$) compared to the number of refining parameters (140).

Results and discussion

The synthesis of **1** was accomplished, in a facile manner, by the metallation of 2,4,6- $\text{Ph}_3\text{C}_6\text{H}_2\text{Br}$ with *n*-BuLi. The reaction proceeds smoothly and in high yield and the product **1** is easily purified by crystallization. The asymmetric unit (Fig. 1) contains a mononuclear structure that is comprised of lithium coordinated to two ethers and the *ipso* carbon of a substituted phenyl ring. The monomeric nature of **1** is presumably due to the replacement of *ortho*-*i*-Pr groups with phenyl substituents which is sufficient to block the dimerization that was observed for $[\{\text{Li}(\text{Et}_2\text{O})\text{Triph}\}_2]$ [3].

The coordination at the lithium center is trigonal planar. The large size of the Triph group is reflected in the O(1)–Li–O(2) angle which is more than 10° less obtuse than either of the C(1)–Li–O angles. A further manifestation of the crowding in the molecule is the large angle (64°) between the C(1) aromatic ring and the LiO(1)O(2) planes. The ionic nature of the Li–C(1) interaction is reflected in the rather low, $111.7(7)^\circ$, internal ring angle at C(1). Attention has already been drawn to narrowness of the angles at the *ipso*-carbons in various organolithium and other metal aryl compounds [9]. The higher negative charge at C(1) also results in C(1)–C(*ortho*) distances that are longer than normal.

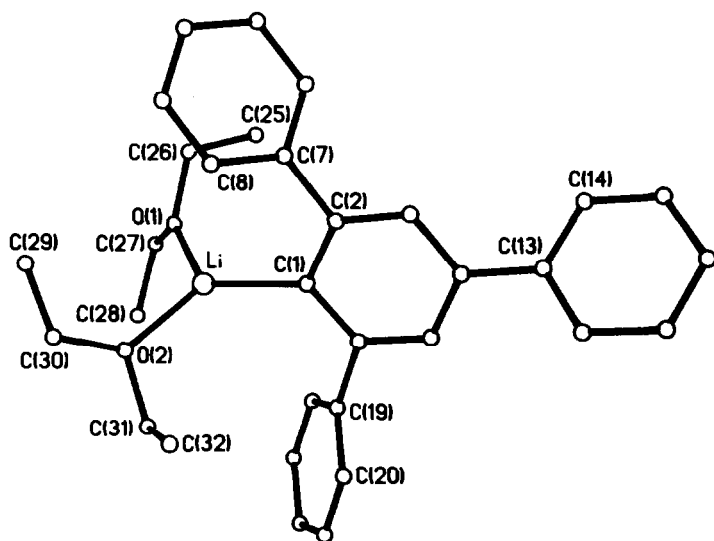


Fig. 1. A drawing of the asymmetric unit of **1**. Selected bond lengths and angles are given in Table 2. H atoms are omitted for clarity.

Table 3

Important structural parameters for some monomeric organolithium compounds

Compound	Li coord. no.	C coord. no.	Li–C (Å)	Ref.
[LiCH(SiMe ₃) ₂]	1	4	2.03(6)	16
[Li(Et ₂ O) ₂ Triph], 1	3	3	2.074(16)	this work
[Li(TMEDA)2,4,6-t-Bu ₃ C ₆ H ₂] ^a	3	3	2.117(9)	9
[Li(THF)C(SiMe ₂ Ph) ₃]	2–3	4	2.12(1)	5
[Li(PMDETA)CH(SiMe ₃) ₂] ^b	4	4	2.13(5)	16
[Li{C(SiMe ₃) ₃] ₂] [–]	2	4	2.18(2)	6
[Li(PMDETA)MeC ₂ B ₁₀ H ₁₀]	4	5	2.18	23
[Li(TMEDA)(THF)C(Ph)S(CH ₂) ₃ S] ^c	4	4	2.28	24
[Li(Et ₂ O) ₂ CPh ₃] ^c	3–5	4	2.306(14)	3

^a TMEDA = tetramethylethylenediamine; ^b PMDETA = pentamethyldiethylenetriamine; ^c contact ion pairs.

The Li–C(1) distance in **1** is only 2.074(16) Å. This is one of the shortest Li–C distances that has been experimentally observed [16]. It is very close to the Li–C distances seen in other low coordinate organolithium compounds. A listing of some monomeric organolithium lithium species and important structural data are provided for comparison in Table 3. Clearly, the Li–C(1) distance is within the range expected on the basis of the relatively low coordination number at Li and C(1). These distances are much shorter than the 2.25–2.35 Å bond lengths seen in normal organolithium derivatives [17]. Such compounds generally have four coordinate lithium and coordination numbers of between four and six for carbon. The Li–O distances, ~1.95 Å, are, on average, at the longer end of the spectrum for three coordinate lithium [16] complexed to ethers. For example, they are longer than the 1.930(3) Å Li–O distances observed in [{Li(Et₂O)Triph}₂] [3], the 1.925 Å in [{Li(Et₂O)PMes₂]₂] [18], the 1.903(14) Å in [Li(Et₂O)₃]⁺ [19] and 1.939(6) Å in [(THF)LiMn{N(SiMe₃)₂]₃] [20]. A similar distance 1.955(9) Å was observed in the structure of [Li(Et₂O)benzyl]_∞ [2] but a comparison with this compound is compromised by a further possible Li–C interaction with an adjacent ring carbon, which changes the effective coordination number at Li⁺ from 3 to 4. The apparent lengthening in the the Li–O distances in **1** may be due to the crowding in the molecule which, as noted already, causes the O–Li–O angle to close somewhat. In addition, a particularly strong Li–C interaction in **1** may weaken the remaining Li–O interactions. There is no evidence for any strong interaction between a C–H moiety from the phenyl group and the lithium center. The closest Li–H approach is 2.82 Å.

There is little evidence for severe crowding in **1**, as judged by the lack of any great distortions of bond lengths and angles within the organic moiety. For example, all the aromatic rings are planar whereas distortions from planarity are often observed in the aromatic ring of derivatives of the similar 2,4,6-t-Bu₃C₆H₂ group [21]. Neither are any major distortions or strains evident in the environment of the *ortho* carbons (C(2) and C(6)) of the C(1) ring. The C(1)–C(2)–C(7) and C(1)–C(6)–C(19) angles are both within 2° of 120°. The C(2)–C(7) and C(6)–C(19) bonds are close to 1.5 Å which is within the range expected for a C–C bond derived from *sp*²–*sp*² overlap [22]. The angles between the C(7), C(19) and C(1) plane can be rationalized on the basis of their orientation with respect to the Li(OEt₂)₂ moiety.

In summary, this paper has described the synthesis and structure of the novel lithium reagent $[\text{Li}(\text{Et}_2\text{O})_2\text{Triph}]$, **1**. In addition, it has been shown that this reagent can be made in high yield by a facile route.

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