Lipophilic Lithium Alkoxides or Dialkylboroxides; *X*-Ray Structures of $[Li(\mu\text{-}OR')]_2$ and $Li(OBR_2)(tmeda)$, [tmeda = $(Me_2NCH_2)_2$, R = $CH(SiMe_3)_2$, R′ = CBu^t_3 or BR_2]†

Gerhard Beck, Peter B. Hitchcock, Michael F. Lappert, and Iain A. MacKinnon

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Treatment of Bu^t_3COH or BR_2OH [R = $CH(SiMe_3)_2$] with $LiBu^n$ yields the colourless crystalline $[Li(\mu\text{-}OR')]_2$, [R′ = CBu^t_3 (**1**) or BR_2 (**2**)]; the dialkylboroxide (**2**) reacts with tmeda [tmeda = $(Me_2NCH_2)_2$], MeCOCl, or $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ to yield $Li(OBR_2)(tmeda)$ (**3**), BR_2OH, or $[Ti(\eta\text{-}C_5H_5)_2(Cl)(OBR_2)]$, respectively; *X*-ray data on complexes (**1**)—(**3**) are compared with those for related LiO compounds, the two-co-ordinate lithium environment in (**1**) and (**2**), and the exceedingly short Li–O [1.677(5) Å] and O–B [1.308(8) Å] distances in (**3**) being noteworthy.

The structures of lithiated organic compounds[1] are of considerable interest from both a synthetic[1] and a theoretical[2] standpoint, and such data are available for numerous LiO compounds. These often have lithium in a four-co-ordinate environment, but a Li co-ordination number (C.N.) of three is relatively rare (Table 1, for alkoxides, aryloxides, and boroxides; for structures of lithium enolates, see ref. 2c);[3—7] other examples of C.N. = 3 for alkoxides are in unusual bimetallic complexes such as $[Cr(OR^1)_2(\mu\text{-}OR^1)_2Li(thf)]$, ($R^1$ = $CHBu^t$, thf = tetrahydrofuran).[8] The lithium is frequently in a solvated cation or a neutral polymer.

We now report on the synthesis (i and ii in Scheme 1) and structures (Table 1 and Figures 1—3) of three novel hydrocarbon-soluble, colourless, crystalline, neutral lithium alkoxides or boroxides: $[Li(\mu\text{-}OCBu^t_3)]_2$ (**1**), $[Li(\mu\text{-}OBR_2)]_2$ (**2**), and $Li(OBR_2)(tmeda)$ (**3**), [R = $CH(SiMe_3)_2$, tmeda = $(Me_2\text{-}$

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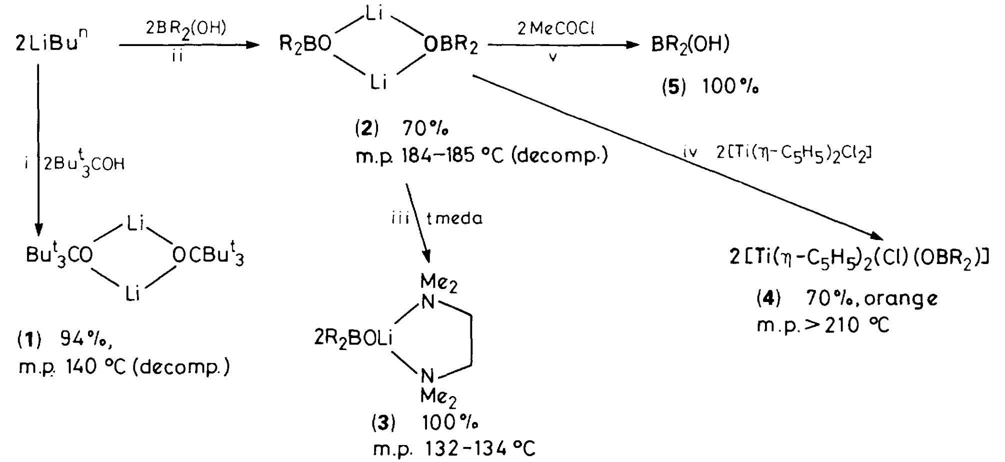
† No reprints available.



Scheme 1. *Abbreviations*: R = CH(SiMe$_3$)$_2$, tmeda = (Me$_2$NCH$_2$)$_2$. *Reaction conditions*: i, n-C$_6$H$_{14}$, *ca.* 25 °C, 12 h, and then −25 °C for 5 h; ii, n-C$_6$H$_{14}$, *ca.* 25 °C, volatiles removed *in vacuo*, extraction into n-C$_6$H$_{14}$, then −20 °C; iii or iv, n-C$_6$H$_{14}$, *ca.* 25 °C, filtration, then filtrate at −20 °C; v, *ca.* 25 °C, 2 h, then extraction into n-C$_6$H$_{14}$, filtration, and filtrate at −20 °C. *Identification procedures*: crystalline compounds (1)—(4) were characterised by microanalysis, ^{1}H, ^{13}C{^{1}H} [not (1)], ^{7}Li{^{1}H} [δ_{Li} 0.85 (1), 0.12 (2), or 0.26 (3) p.p.m. relative to external standard, aq. LiNO$_3$], or ^{11}B{^{1}H} [δ_B 49.0 (2), 42.5 (3), or 53.4 (4) p.p.m., relative to external standard BF$_3$(OEt$_2$)] n.m.r. (C$_6$D$_5$CD$_3$ at 30 °C), and in the case of (1)—(3) by *X*-ray diffraction (Figures 1—3).

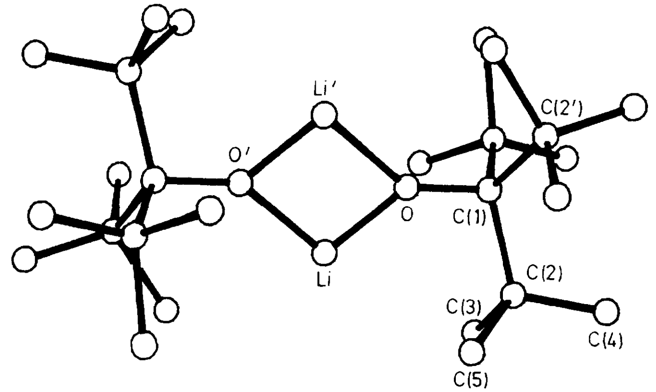


Figure 1. *X*-Ray structure of (1), [Li(μ-OCBu$^t_3$)]$_2$, with numbering scheme.

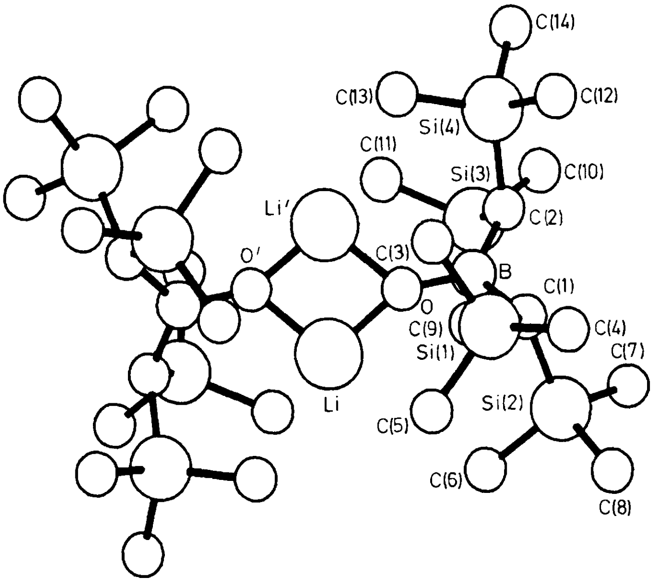


Figure 2. *X*-Ray structure of (2), [Li(μ-OCBR$_2$)]$_2$, [R = CH(SiMe$_3$)$_2$], with numbering scheme.

NCH$_2$)$_2$].‡ Compounds (1) and (2) have the unprecedented (in a monometallic compound) C.N. of two for Li, and have very short Li · · · Li distances: 2.19(12) and 2.21(2) Å, respectively, *cf.* 2.342 Å in [Li(μ-OCBu$^t_3$)(thf)]$_2$,[5] but 2.20(1) Å at the ends of the Li$_8$ cluster [*o*-LiC$_6$H$_4$CH$_2$N-Li(CH$_2$CH$_2$NMe$_2$)]$_4$.[9] The monomeric compound (3) has by far the shortest Li–O bond. The B–O bond length in (3) is also remarkably short, and the oxygen lone pairs are stereochemically inactive, bond angle, Li–O–B = 173.9(7)°; each of these three features points to significant $\overset{\frown}{\mathrm{O}\text{–}\mathrm{B}}$ p$_\pi$ interaction. Compound (2) showed a close Li · · · CH$_3$ contact.

Two bimetallic complexes having two-co-ordinate lithium are known: [Mn{N(SiMe$_3$)$_2$}(μ-OCBu$^t_3$)$_2$Li] and [Li(thf)$_2$(μ-Br)$_2$Mn(μ-OCBu$^t_3$)$_2$Li]; the Li(sp)–O distances were 1.808(14) and 1.816(21) Å, respectively, and both compounds also showed a close Li · · · CH$_3$ interaction of 2.52(3) and 2.46(3) Å, respectively.[10] The only crystalline compound other than (1) or (2) of structure [Li(μ-X)]$_2$ has X = PR$_2$.[11]

Three reactions (iii—v in Scheme 1) of [Li(μ-OBR$_2$)]$_2$ (2)

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‡ *Crystal data* for (1) {(2)}[(3)]: C$_{26}$H$_{54}$Li$_2$O$_2$ {C$_{28}$H$_{76}$B$_2$Li$_2$O$_2$Si$_8$} [C$_{20}$H$_{54}$BLiN$_2$OSi$_4$], *M* = 412.6 {705.1}[468.8], cubic {monoclinic} [monoclinic], space group *Pa*3 {*C*2/*c*}[*P*2$_1$/*n*], *a* = 13.856(7) {24.467(7)}[9.246(10)], *b* = {10.925(2)}[17.008(10)], *c* = {18.169(7)}[21.089(9)] Å, β = {94.84(3)}[95.99(6)]°, *U* = 2660.2 {4839.4}[3298.1] Å^3, *Z* = 4{4}[4], D_c = 1.03 {0.97}[0.94] g cm^{-3}. Monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 0.6{2.4}[1.9] cm^{-1}. Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size *ca.* 0.3 × 0.3 × 0.2 {1.0 × 0.3 × 0.3}[0.5 × 0.3 × 0.3] mm sealed in a Lindemann capillary under argon. There was no crystal decay during collection.

For (1), diffraction data became very weak for higher angle reflections. Intensities for 1506 {3640}[4191] reflections were measured for +*h*, +*k*, +*l* {+*h*, +*k*, ±*l*}[+*h*, +*k*, ±*l*] and $2 < \theta < 20°$ {$2 < \theta < 23°$}[$2 < \theta < 22°$]; of these 196 {1244}[2254] unique reflections with $|F^2| > \sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (PI)^2]^{\frac{1}{2}}/L_p$, [*P* = 0.02 for (1) and *P* = 0.04 for (2) or (3)].

The structures were solved by routine direct methods using MULTAN and refined by full-matrix least-squares; non-hydrogen atoms anisotropic and hydrogen atoms at fixed positions, with $B_{iso} = 1.3B_{eq}$ for the C atom to which they are bonded, or omitted for (1). The weighting scheme was $w = 1/\sigma^2(F)$ and *R* = 0.105 {0.065}[0.087] and R_w = 0.113 {0.067}[0.101]. In (1) the Li atoms are disordered between six equivalent positions.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Selected *X*-ray structure data on lithium alkoxides and boroxides.

Empirical formula[a]		n in crystalline $(LiOR)_n$	Co-ordination number of Li	<Li–O> /Å	<O–C> or [<O–B>]/Å	∠LiOLi/°	∠OLiO/°	Ref.
LiOMe		∞	4	1.95	1.42	80.3	101.7, 131.1	3
$LiOCBu^t_2CH_2PMe_2$		2	3[b]	1.78(1)	1.385(6)	80.1(5)	99.9(5)	4
$LiOCBu^t_2CH_2PPh_2$		2	3[b]	1.792(7)	1.384(7)	81.9(3)	98.1(3)	4
$LiOCBu^t_3$(thf)		2	3	1.84(1)	1.392(7)	79.3(5)	98.7(4)	5
$LiOCBu^t_3$	(**1**)	2	2	1.75(8)	1.387(13)	77(3)	103(3)	—[c,d]
$LiOAr(OEt_2)$		2	3	1.86(1)	1.34(1)	83.8(4)	96.2(4)	6
$LiOBMes_2$(thf)		2	3	1.849(7)	[1.317(6)]	83.2(3)	96.6(5), 97.1(5)	7
$LiOBR_2$	(**2**)	2	2	1.78(2)	[1.345(9)]	77.0(8)	102.9(8)	—[c,e]
$LiOBR_2$(tmeda)	(**3**)	1	3	1.677(15)	[1.308(8)]	—	—	—[c,f]

[a] *Abbreviations*: R = $CH(SiMe_3)_2$; Mes = $C_6H_2Me_3$-2,4,6; Ar = $C_6H_2Bu^t_2$-2,6-Me-4; thf = OC_4H_8; tmeda = $(Me_2NCH_2)_2$. [b] One of the co-ordination sites is occupied by P. [c] This work. [d] Li–O 1.83(3), Li–O′ 1.67(8), O–C(1) 1.387(13) Å; C(1)OLi 139(1), C(1)OLi′ 144(3), OC(1)C(2) 106.1(5)°. [e] Li–O 1.75(2), Li–O′ 1.80(2), B–C(1) 1.588(11), B–C(2) 1.593(11), Li · · · C(13) 2.63(2), Li · · · C(11) 3.23(2) Å; LiOB 151.7(7), Li′OB 131.3(7), OBC(1) 120.6(6), OBC(2) 118.8(7), C(1)BC(2) 120.5(6)°. [f] Li–N(1) 2.13(2), Li–N(2) 2.08(2), B–C(1) 1.634(10), B–C(2) 1.632(10) Å; LiOB 173.9(7), OBC(1) 121.0(6), OBC(2) 120.6(6), C(1)BC(2) 118.4(6)°.

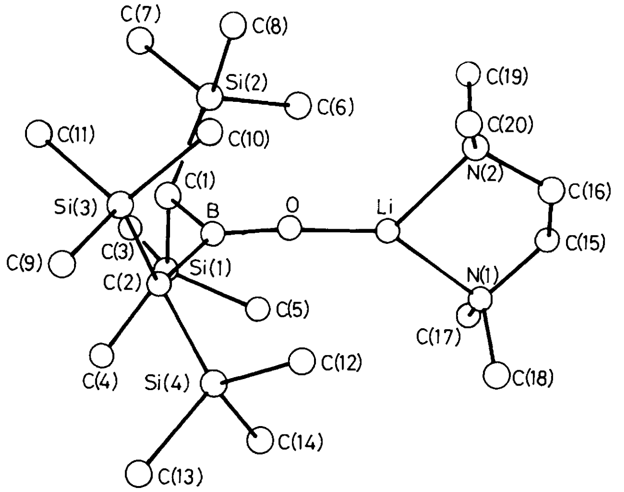

Figure 3. *X*-Ray structure of (**3**), $Li(OBR_2)$(tmeda), [R = $CH(SiMe_3)_2$, tmeda = $(Me_2NCH_2)_2$], with numbering scheme.

illustrate its versatility. Its behaviour as a lithium-centred Lewis acid is shown by the formation of 1 : 1 tmeda adduct (**3**). Compound (**2**) acts as an *O*-centred nucleophile in its reaction with $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ to yield $[Ti(\eta\text{-}C_5H_5)_2(Cl)(OBR_2)]$ (**4**); the second Cl^- ligand is not replaceable by the bulky $^-OBR_2$. Finally, compound (**2**) functions as a strong Brønsted base in dehydrochlorinating acetyl chloride under ambient conditions to yield $BR_2(OH)$[11] (**5**)§ (and presumably CH_2=C=O as a co-product).

Power and co-workers have shown that $Li(OCBu^t_3)$(thf) is likewise a useful *O*-centred nucleophile,[5,10] and corresponding alkoxides ('tritoxides')[12] are known for a number of transition,[5,12] main group (Ge^{II} and Sn^{II}),[13] and f-block[14] metals. Compound (**1**) and $Ge(OCBu^t_3)_2$ [13] are isomorphous. The latter was made from $Ge[N(SiMe_3)_2]_2$ plus $2Bu^t_3COH$; similarly $Na[N(SiMe_3)_2]$ or '$MgBu_2$'[15] and tri-t-butylmethanol in n-C_6H_{14} have now been shown at ambient temperature to yield the hydrocarbon-soluble, colourless, crystalline $Na(OCBu^t_3)$ (**6**)§ or $Mg(OCBu^t_3)_2$ (**7**),§ respectively.

Compounds (**2**)—(**4**) are only the second group of a potentially useful family of compounds containing a boroxide ligand, having been preceded by the bis(mesityl)boroxides of Power and co-workers: $[Li(\mu\text{-}OBMes_2)(thf)]_2$ and $[Li(thf)_2(\mu\text{-}OBMes_2)_2Co(\mu\text{-}Cl)_2Li(thf)_2]$ (Mes = $C_6H_2Me_3$-2,4,6).[7]

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§ $BR_2(OH)$ (**5**) was made by hydrolysis of BR_2Cl (**5a**) [R = $CH(SiMe_3)_2$].[16] *Characterisation of crystalline compounds* (**5**)—(**7**). (**5a**), m.p. 100—101 °C, n.m.r. ($CDCl_3$, 300 K): ^1H δ 1.01 (CH), 0.15 (Me); $^{13}C\{^1H\}$ δ 32.0 (CH), 2.6 (Me); $^{11}B\{^1H\}$ δ_B 70.6 p.p.m. (**5**), m.p. 51—52 °C, i.r. (Nujol) ν(OH) 3643 cm^{-1}, n.m.r. (C_6D_6, 300 K): ^1H δ 4.35 (OH), 0.29 (CH), 0.15 (Me); $^{13}C\{^1H\}$ δ 22.4 (CH), 2.8 (Me); $^{11}B\{^1H\}$ δ_B 53.7 p.p.m. (**6**), m.p. 128—130 °C (decomp.), ^1H n.m.r. (C_6D_6, 300 K) δ 1.40. (**7**), m.p. *ca.* 117 °C (decomp.), ^1H n.m.r. (C_6D_6, 300 K) δ 1.46.