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Supporting Information

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Pure α-Metallated Benzyllithium From a Single-Crystal-to-Single-Crystal Transition**

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Fig. 1 Superposition of ^{1}H-DOSY NMR spectra of [{$Me_2N(CH_2)_2OMe$}·($LiCH_2SiMe_3$)]$_2$ (**2**, blue) and $Me_2N(CH_2)_2OMe$ (red) showing the diffusion constants D in logarithmic scale [m^2s^{-1}].
$LiCH_2SiMe_3$ log D/m^2s^{-1} = –9.01
($Me_2N(CH_2)_2OMe$) log D/m^2s^{-1} = –8.96

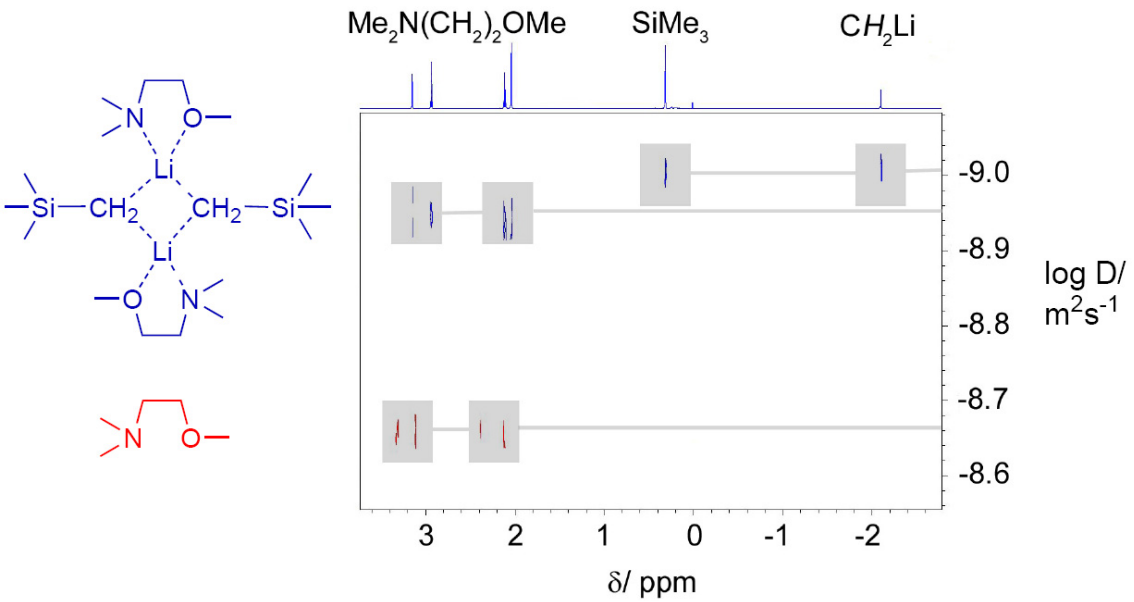


Fig. 2 ^{1}H-DOSY NMR spectrum of [{$Me_2N(CH_2)_2OMe$}·($LiCH_2Ph$)]$_4$ (**3**)
$LiCH_2Ph$ log D/m^2s^{-1} = –9.04
$Me_2N(CH_2)_2OMe$ log D/m^2s^{-1} = –8.98
TMS log D/m^2s^{-1} = –8.63

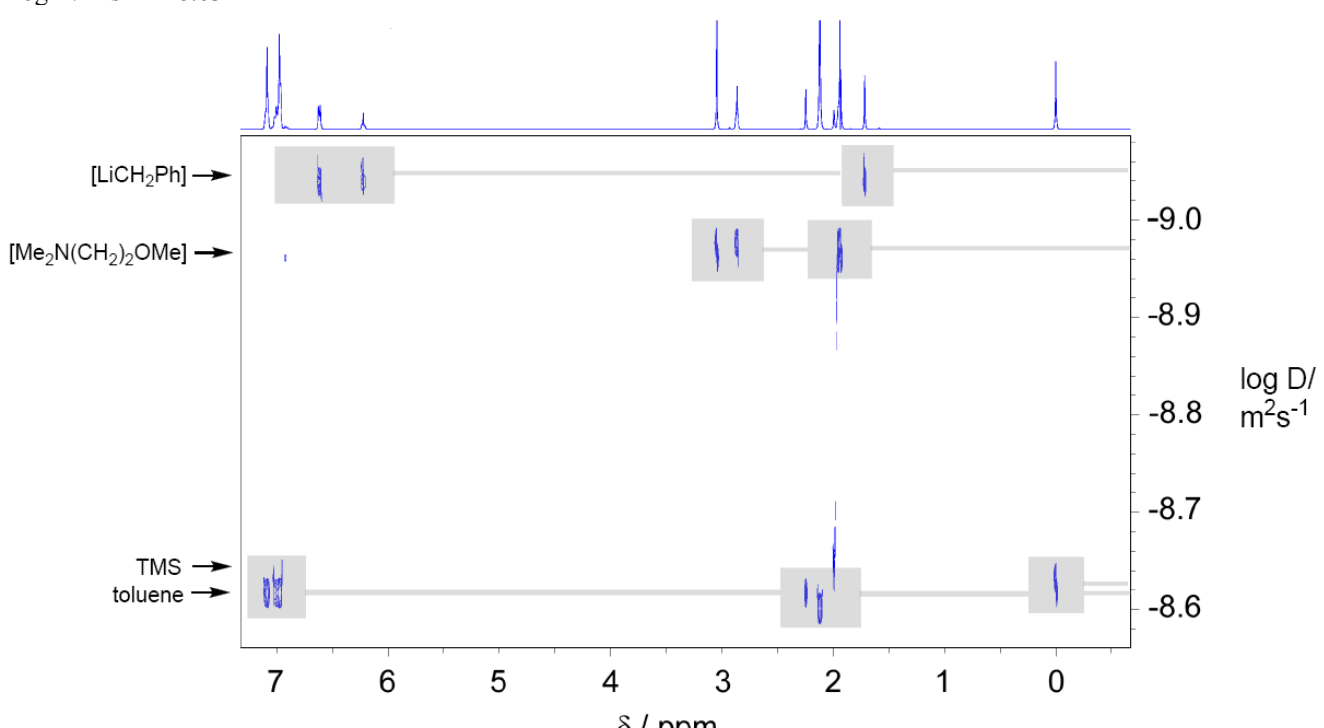


Fig. 3 ^{1}H NMR spectra of the reaction of [{$Me_2N(CH_2)_2OMe$}·($LiCH_2SiMe_3$)]$_2$ (**2**) to [{$Me_2N(CH_2)_2OMe$}·($LiCH_2Ph$)]$_4$ (**3**). The spectra were measured every 24 h and show the decreasing of the signals of **2** and increasing of signals of **3**.

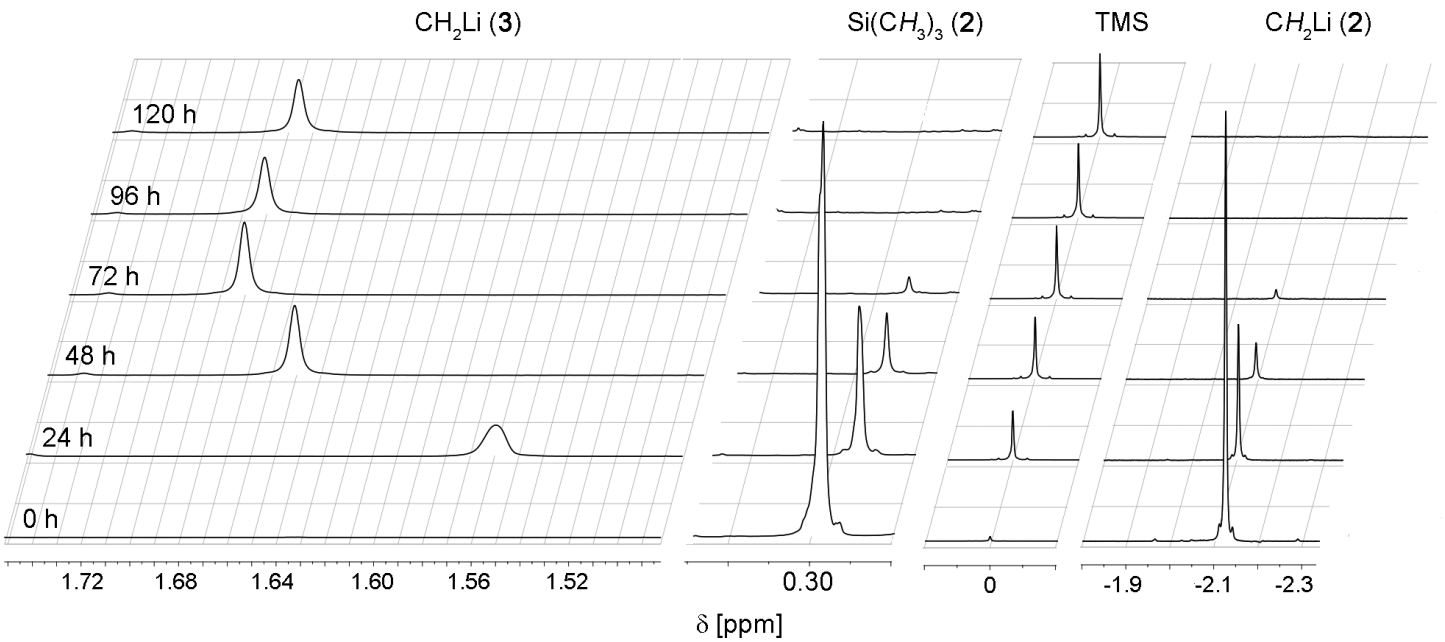


Fig. 4 ^{1}H NMR spectrum of [{$Me_2N(CH_2)_2OMe$}·($LiCH_2Ph$)]$_4$ (**3**) showing the $^{1}J_{(H,C)}$ coupling (127 Hz) of the C_α atom.

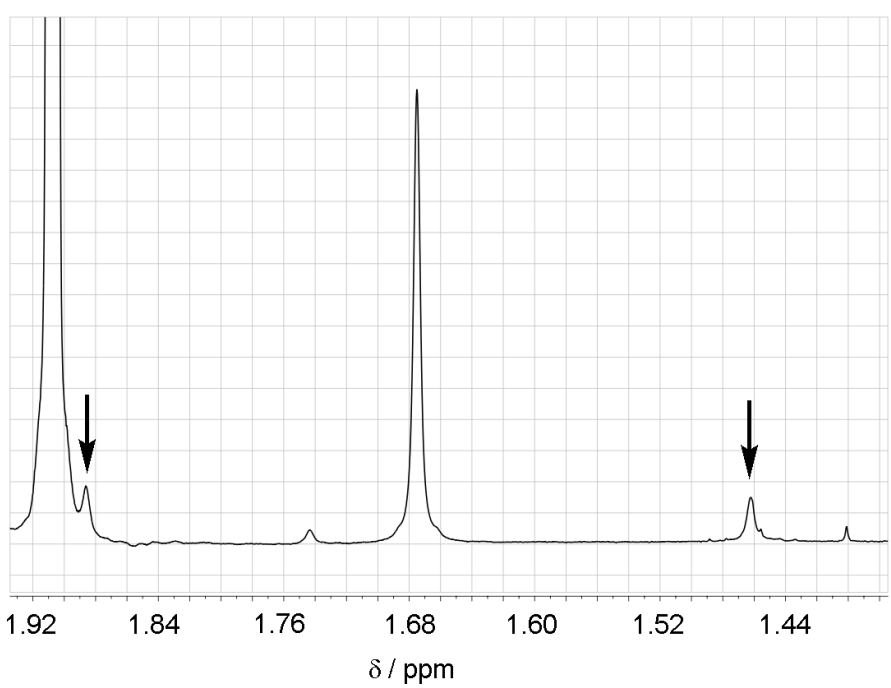
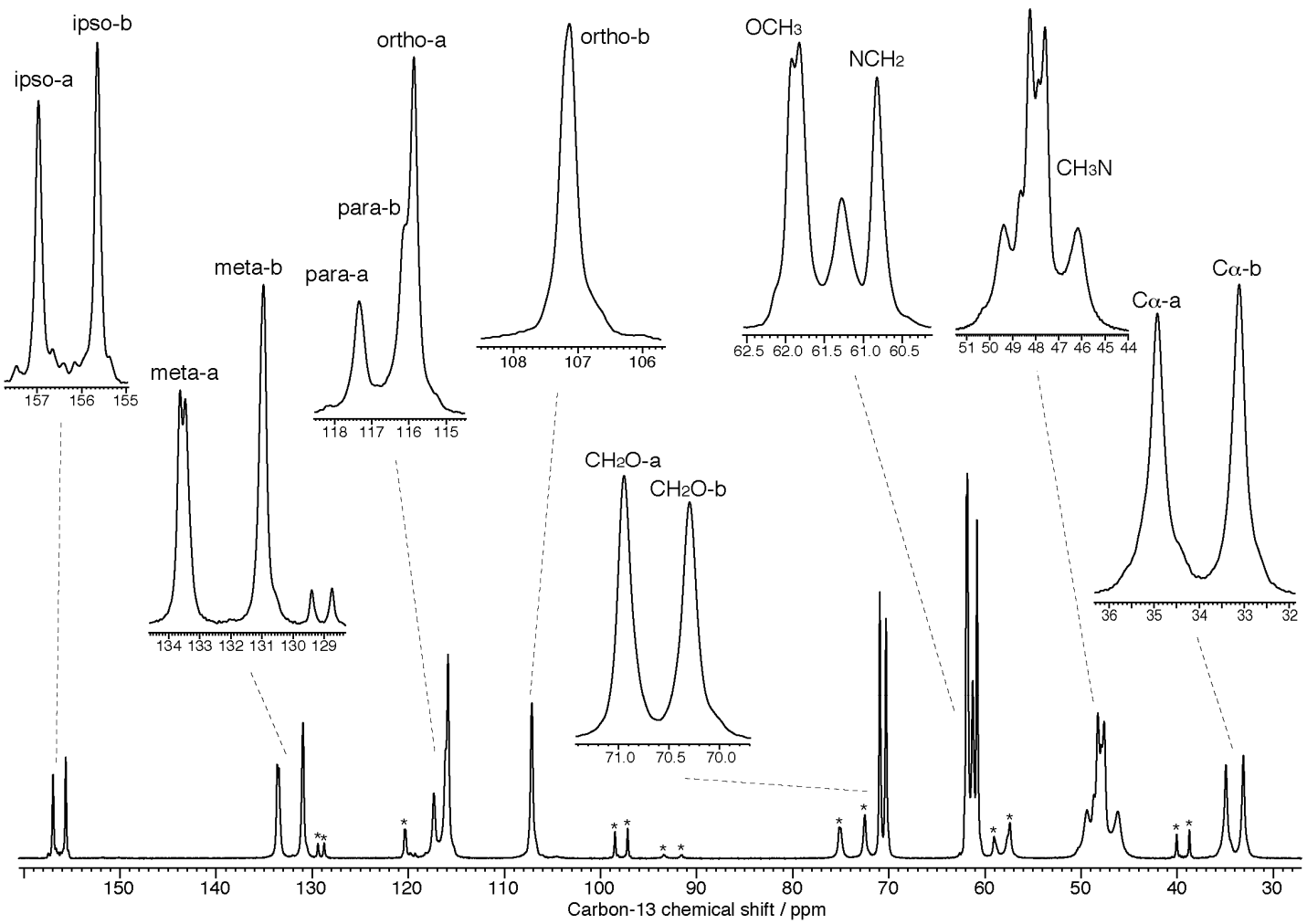


Fig. 5 Solid state ^{13}C NMR spectrum of $[\{Me_2N(CH_2)_2OMe\}\cdot(LiCH_2Ph)]_4$ (**3,** * indicate spinning side bands)

Conditions:

The solid state nuclear magnetic resonance experiment was carried out on sample **3**. The sample was packed under argon atmosphere in a 4 mm MAS rotor. The ^{1}H to ^{13}C cross-polarization (CP) experiment was conducted on a 20.0 Tesla (^{1}H resonance frequency: 850 MHz) wide-bore spectrometer (Bruker Biospin, Germany), equipped with a 4 mm triple-resonance MAS probe. The spectrum was recorded at a spinning frequency of 12.5 kHz, using high-power ^{1}H-^{13}C decoupling with a radio-frequency amplitude of 90 kHz during acquisition. A ramped cross-polarization was used to transfer magnetization from ^{1}H to ^{13}C during a contact time of 1.75 ms. An acquisition time of 50 ms was used for 10.240 scans (total experimental time of 14 hours). The spectrum was Fourier-transformed without any apodization function. Chemical shifts were referenced using DSS.



Single-crystal structural analysis:

Table 1. Crystal data and structure refinement for **2**, **3** and **4**:

Compound	$[\{Me_2N(CH_2)_2OMe\}\cdot(LiCH_2SiMe_3)]_2$ (2)	$[\{Me_2N(CH_2)_2OMe\}\cdot(LiCH_2Ph)]_4$ (3)	$[(PMDETA)\cdot(LiCH_2Ph)]$ (4)
Empirical formula	$Li_2C_{18}H_{48}N_2O_2Si_2$	$Li_4C_{48}H_{80}N_4O_4$	$LiC_{16}H_{30}N_3$
CCDC no.	818468	818338	818339
Molecular weight	394.64	804.92	271.37
Crystal size [mm]	0.20 x 0.10 x 0.05	0.30 x 0.10 x 0.10	0.30 x 0.10 x 0.08
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a [pm]	761.90(7)	2429.0(5)	1538.8(10)
b [pm]	1851.42(16)	889.00(18)	1337.9(8)
c [pm]	980.57(9)	2452.9(5)	1706.8(11)
β [°]	100.5560(10)	111.23(3)	93.381(11)
V [nm^3]	1.3598(2)	4.9355(17)	3.51(1)
Z	2	4	8
Temperature [K]	100(2)	100(2)	100(2)
ρ [Mgm^{-3}]	0.964	1.083	1.028
μ [mm^{-1}]	0.142	0.066	0.060
F (000)	440	1760	1200
θ-area [°]	2.20 to 27.48	1.78 to 29.93	1.33 to 21.65
Total number reflect.	26481	64798	31672
Unique reflections	3113	6888	4068
Number of restraints	0	175	0
Parameters	132	342	387
R1 [I>2σ(I)]	0.0332	0.0452	0.0500
wR2 [I>2σ(I)]	0.0869	0.1190	0.1198
R1 [all data]	0.0366	0.0577	0.0682
wR2 [all data]	0.0893	0.1281	0.1298
GooF	1.085	1.058	1.078
Largest diff. peak / hole max. / min. [e.Å^{-3}]	0.325 and –0.184	0.410 and –0.385	0.270 and –0.208

[{$Me_2N(CH_2)_2OMe$}·($LiCH_2SiMe_3$)]$_2$ (2):

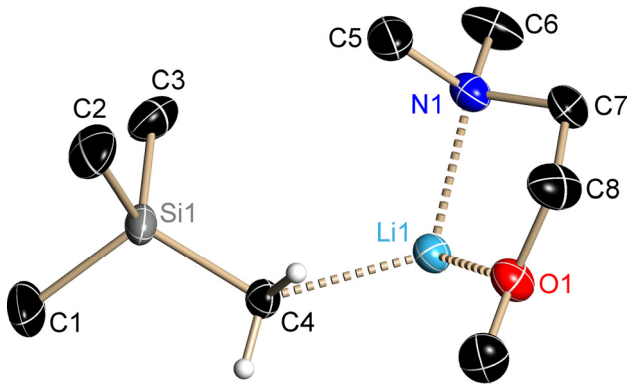


Figure 6 Molecular structure of [{$Me_2N(CH_2)_2OMe$}·($LiCH_2SiMe_3$)]$_2$ (**2**) in the crystal (asymmetric unit). Anisotropic displacement parameters are depicted at the 50 % probability level.

Table 2. Bond lengths [Å] and angles [°] for **1**.

Si(1)-C(4)	182.49(11)	C(1)-Si(1)-C(3)	104.91(8)
Si(1)-C(1)	188.57(14)	C(4)-Si(1)-C(2)	114.70(6)
Si(1)-C(3)	188.81(14)	C(1)-Si(1)-C(2)	105.56(7)
Si(1)-C(2)	189.34(13)	C(3)-Si(1)-C(2)	104.64(7)
Li(1)-O(1)	205.7(2)	O(1)-Li(1)-N(1)	82.13(7)
Li(1)-N(1)	215.2(2)	O(1)-Li(1)-C(4)#1	118.63(9)
Li(1)-C(4)#1	221.4(2)	N(1)-Li(1)-C(4)#1	115.19(9)
Li(1)-C(4)	223.6(2)	O(1)-Li(1)-C(4)	107.91(9)
Li(1)-Li(1)#1	242.9(3)	N(1)-Li(1)-C(4)	115.38(9)
Li(1)-H(12)	208.3(16)	C(4)#1-Li(1)-C(4)	113.84(8)
N(1)-C(5)	145.94(15)	O(1)-Li(1)-Li(1)#1	136.04(13)
N(1)-C(6)	146.80(15)	N(1)-Li(1)-Li(1)#1	141.50(13)
N(1)-C(7)	147.15(16)	C(4)#1-Li(1)-Li(1)#1	57.35(8)
O(1)-C(8)	142.14(14)	C(4)-Li(1)-Li(1)#1	56.49(8)
O(1)-C(9)	142.46(14)	O(1)-Li(1)-H(12)	85.0(4)
C(4)-Li(1)#1	221.4(2)	N(1)-Li(1)-H(12)	100.4(5)
C(4)-H(11)	93.3(17)	C(4)#1-Li(1)-H(12)	138.7(5)
C(4)-H(12)	99.0(16)	C(4)-Li(1)-H(12)	26.2(5)
C(7)-C(8)	150.25(19)	Li(1)#1-Li(1)-H(12)	81.9(5)
		C(5)-N(1)-C(6)	109.28(11)
C(4)-Si(1)-C(1)	113.11(6)	C(5)-N(1)-C(7)	110.30(10)
C(4)-Si(1)-C(3)	113.01(6)	C(6)-N(1)-C(7)	109.97(10)

C(5)-N(1)-Li(1)	113.69(9)
C(6)-N(1)-Li(1)	112.74(9)
C(7)-N(1)-Li(1)	100.56(8)
C(8)-O(1)-C(9)	112.90(10)
C(8)-O(1)-Li(1)	113.24(9)
C(9)-O(1)-Li(1)	124.71(9)
Si(1)-C(4)-Li(1)#1	113.35(7)
Si(1)-C(4)-Li(1)	130.95(7)
Li(1)#1-C(4)-Li(1)	66.16(8)
Si(1)-C(4)-H(11)	107.5(10)
Li(1)#1-C(4)-H(11)	87.7(10)
Li(1)-C(4)-H(11)	121.3(10)
Si(1)-C(4)-H(12)	107.5(9)
Li(1)#1-C(4)-H(12)	131.9(9)
Li(1)-C(4)-H(12)	68.2(9)
H(11)-C(4)-H(12)	103.4(13)
N(1)-C(7)-C(8)	112.05(10)
O(1)-C(8)-C(7)	108.04(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

[{$Me_2N(CH_2)_2OMe$}·($LiCH_2Ph$)]$_4$ (3):

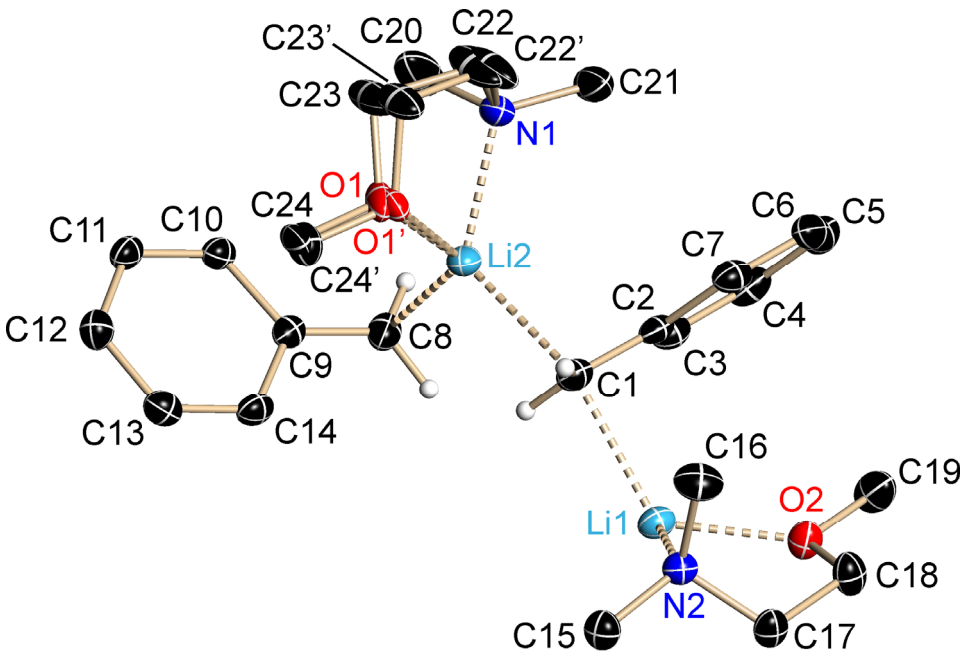


Figure 7 Molecular structure of [{$Me_2N(CH_2)_2OMe$}·($LiCH_2Ph$)]$_4$ (**3**) in the crystal (asymmetric unit) including disordered sites. Anisotropic displacement parameters are depicted at the 50 % probability level.

Table 3. Bond lengths [Å] and angles [°] for **3**.

Li(2)-O(1')	202.4(4)	C(1)-H(901)	96.0(16)
Li(2)-O(1)	205.4(7)	C(1)-H(900)	96.2(18)
Li(2)-N(1)	212.2(2)	C(3)-C(4)	137.8(2)
Li(2)-C(8)	230.9(2)	C(7)-C(6)	137.9(2)
Li(2)-C(1)	231.5(2)	C(4)-C(5)	139.4(2)
Li(2)-C(2)	276.7(2)	C(6)-C(5)	139.1(2)
Li(2)-H(901)	222.1(16)	C(10)-C(11)	138.54(18)
Li(1)-O(2)	202.2(2)	C(10)-C(9)	143.32(16)
Li(1)-N(2)	215.4(2)	C(14)-C(13)	138.13(19)
Li(1)-C(1)	228.9(2)	C(14)-C(9)	142.98(17)
Li(1)-C(8)#1	231.4(2)	C(8)-C(9)	141.57(17)
Li(1)-C(2)	267.9(2)	C(8)-Li(1)#1	231.4(2)
Li(1)-C(9)#1	276.9(2)	C(8)-H(903)	98.3(17)
C(2)-C(1)	141.40(18)	C(8)-H(902)	94.4(17)
C(2)-C(7)	143.14(17)	C(9)-Li(1)#1	276.9(2)
C(2)-C(3)	143.21(17)	C(11)-C(12)	139.63(18)

C(13)-C(12)	139.63(18)	C(8)-Li(2)-H(901)	86.4(4)
N(2)-C(16)	146.57(15)	C(1)-Li(2)-H(901)	24.3(4)
N(2)-C(15)	146.92(15)	C(2)-Li(2)-H(901)	47.9(4)
N(2)-C(17)	146.94(15)	O(2)-Li(1)-N(2)	82.48(8)
O(2)-C(18)	141.68(14)	O(2)-Li(1)-C(1)	125.65(11)
O(2)-C(19)	142.98(15)	N(2)-Li(1)-C(1)	107.70(10)
C(17)-C(18)	150.88(17)	O(2)-Li(1)-C(8)#1	104.84(10)
N(1)-C(21)	145.47(16)	N(2)-Li(1)-C(8)#1	127.86(11)
N(1)-C(20)	146.27(18)	C(1)-Li(1)-C(8)#1	108.42(10)
N(1)-C(22')	146.8(3)	O(2)-Li(1)-C(2)	95.94(9)
N(1)-C(22)	147.1(3)	N(2)-Li(1)-C(2)	119.37(9)
O(1)-C(23)	142.2(3)	C(1)-Li(1)-C(2)	31.86(5)
O(1)-C(24)	142.7(4)	C(8)#1-Li(1)-C(2)	111.21(9)
C(22)-C(23)	152.9(3)	O(2)-Li(1)-C(9)#1	111.89(9)
O(1')-C(23')	141.3(3)	N(2)-Li(1)-C(9)#1	98.06(9)
O(1')-C(24')	142.6(3)	C(1)-Li(1)-C(9)#1	118.77(9)
C(22')-C(23')	151.9(3)	C(8)#1-Li(1)-C(9)#1	30.70(5)
		C(2)-Li(1)-C(9)#1	136.13(9)
O(1')-Li(2)-O(1)	6.6(5)	C(1)-C(2)-C(7)	123.22(11)
O(1')-Li(2)-N(1)	83.55(10)	C(1)-C(2)-C(3)	122.85(11)
O(1)-Li(2)-N(1)	82.97(13)	C(7)-C(2)-C(3)	113.93(12)
O(1')-Li(2)-C(8)	124.6(2)	C(1)-C(2)-Li(1)	58.71(8)
O(1)-Li(2)-C(8)	118.6(3)	C(7)-C(2)-Li(1)	111.94(9)
N(1)-Li(2)-C(8)	110.44(10)	C(3)-C(2)-Li(1)	101.14(9)
O(1')-Li(2)-C(1)	103.75(19)	C(1)-C(2)-Li(2)	56.71(8)
O(1)-Li(2)-C(1)	109.5(3)	C(7)-C(2)-Li(2)	123.30(9)
N(1)-Li(2)-C(1)	124.75(11)	C(3)-C(2)-Li(2)	92.73(9)
C(8)-Li(2)-C(1)	109.11(10)	Li(1)-C(2)-Li(2)	110.24(8)
O(1')-Li(2)-C(2)	119.2(2)	C(2)-C(1)-Li(1)	89.43(9)
O(1)-Li(2)-C(2)	125.8(3)	C(2)-C(1)-Li(2)	92.59(9)
N(1)-Li(2)-C(2)	97.99(9)	Li(1)-C(1)-Li(2)	151.99(10)
C(8)-Li(2)-C(2)	111.64(9)	C(2)-C(1)-H(901)	121.6(10)
C(1)-Li(2)-C(2)	30.70(5)	Li(1)-C(1)-H(901)	82.9(9)
O(1')-Li(2)-H(901)	111.8(4)	Li(2)-C(1)-H(901)	72.3(9)
O(1)-Li(2)-H(901)	115.7(5)	C(2)-C(1)-H(900)	120.5(11)
N(1)-Li(2)-H(901)	145.8(4)	Li(1)-C(1)-H(900)	99.8(10)

Li(2)-C(1)-H(900)	103.2(10)
H(901)-C(1)-H(900)	117.8(15)
C(4)-C(3)-C(2)	122.72(12)
C(6)-C(7)-C(2)	122.48(12)
C(3)-C(4)-C(5)	121.57(13)
C(7)-C(6)-C(5)	121.87(13)
C(6)-C(5)-C(4)	117.42(13)
C(11)-C(10)-C(9)	122.25(11)
C(13)-C(14)-C(9)	122.55(11)
C(9)-C(8)-Li(2)	95.78(9)
C(9)-C(8)-Li(1)#1	92.71(9)
Li(2)-C(8)-Li(1)#1	169.28(9)
C(9)-C(8)-H(903)	120.6(10)
Li(2)-C(8)-H(903)	86.9(10)
Li(1)#1-C(8)-H(903)	83.1(10)
C(9)-C(8)-H(902)	122.9(10)
Li(2)-C(8)-H(902)	94.2(10)
Li(1)#1-C(8)-H(902)	86.6(10)
H(903)-C(8)-H(902)	116.0(14)
C(8)-C(9)-C(14)	122.56(11)
C(8)-C(9)-C(10)	122.97(11)
C(14)-C(9)-C(10)	114.47(11)
C(8)-C(9)-Li(1)#1	56.58(8)
C(14)-C(9)-Li(1)#1	105.95(9)
C(10)-C(9)-Li(1)#1	109.20(9)
C(10)-C(11)-C(12)	121.50(11)
C(14)-C(13)-C(12)	121.48(12)
C(11)-C(12)-C(13)	117.73(12)
C(16)-N(2)-C(15)	109.18(10)
C(16)-N(2)-C(17)	110.87(10)
C(15)-N(2)-C(17)	109.46(9)
C(16)-N(2)-Li(1)	110.10(10)
C(15)-N(2)-Li(1)	116.73(9)
C(17)-N(2)-Li(1)	100.19(9)
C(18)-O(2)-C(19)	111.93(10)
C(18)-O(2)-Li(1)	114.39(9)
C(19)-O(2)-Li(1)	129.14(10)
N(2)-C(17)-C(18)	112.33(10)
O(2)-C(18)-C(17)	107.28(10)
C(21)-N(1)-C(20)	109.60(13)
C(21)-N(1)-C(22')	107.00(17)
C(20)-N(1)-C(22')	112.3(3)
C(21)-N(1)-C(22)	113.2(2)
C(20)-N(1)-C(22)	105.9(4)
C(22')-N(1)-C(22)	7.3(4)
C(21)-N(1)-Li(2)	119.54(10)
C(20)-N(1)-Li(2)	106.96(11)
C(22')-N(1)-Li(2)	101.2(2)
C(22)-N(1)-Li(2)	100.5(3)
C(23)-O(1)-C(24)	111.8(5)
C(23)-O(1)-Li(2)	109.4(4)
C(24)-O(1)-Li(2)	131.1(7)
N(1)-C(22)-C(23)	107.1(4)
O(1)-C(23)-C(22)	104.2(4)
C(23')-O(1')-C(24')	113.0(4)
C(23')-O(1')-Li(2)	114.2(2)
C(24')-O(1')-Li(2)	124.1(5)
N(1)-C(22')-C(23')	113.9(3)
O(1')-C(23')-C(22')	107.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,y,-z+1/2

[(PMDETA)·(LiCH$_2$Ph)] (4):

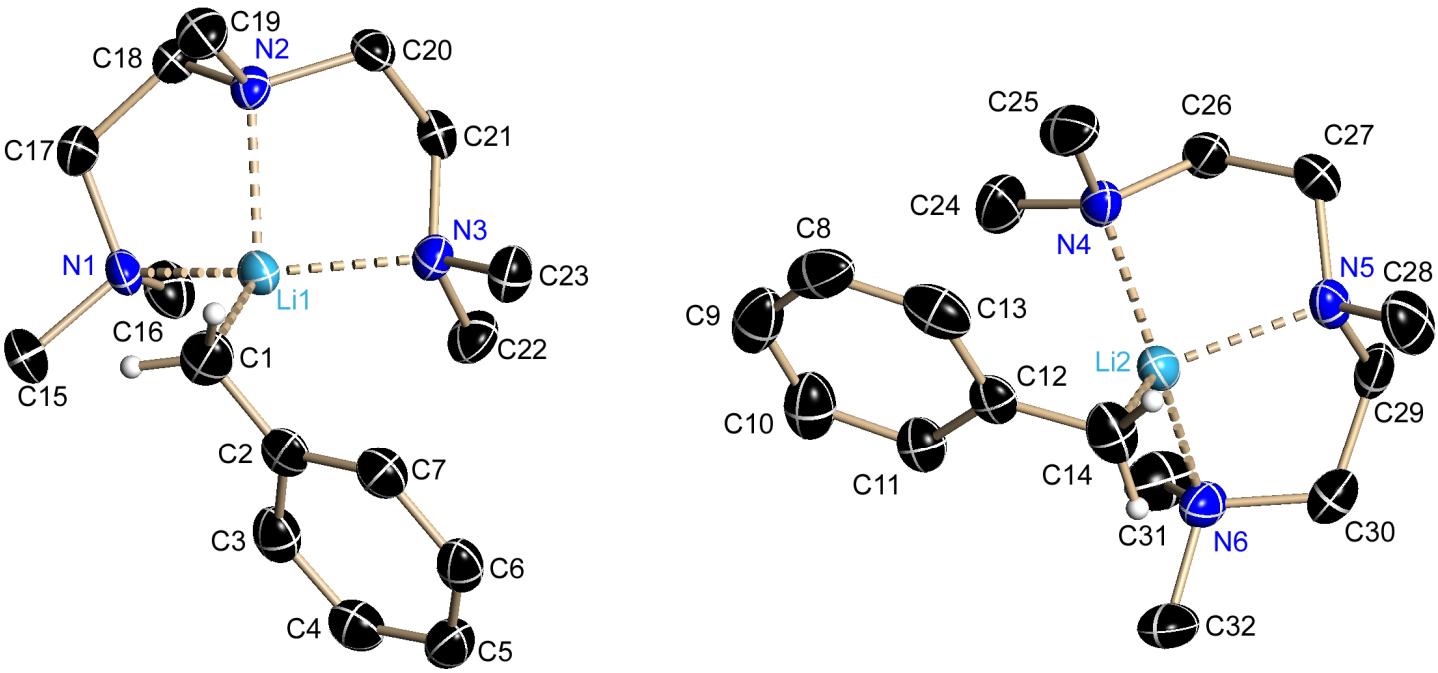


Figure 8 Molecular structure of [(PMDETA)·(LiCH$_2$Ph)]$_2$ (**4**) in the crystal (asymmetric unit). Anisotropic displacement parameters are depicted at the 50 % probability level.

Table 4. Bond lengths [Å] and angles [°] for **4**.

C(6)-C(7)	138.5(4)	C(11)-C(10)	136.6(4)
C(6)-C(5)	138.9(4)	C(14)-Li(2)	221.4(5)
C(2)-C(1)	140.6(4)	C(14)-H(103)	99(3)
C(2)-C(7)	142.4(4)	C(14)-H(102)	104(3)
C(2)-C(3)	143.6(4)	C(10)-C(9)	137.1(4)
C(2)-Li(1)	269.3(5)	C(13)-C(8)	140.7(5)
C(4)-C(3)	137.8(4)	C(9)-C(8)	138.0(5)
C(4)-C(5)	138.9(4)	C(17)-N(1)	148.1(3)
C(1)-Li(1)	220.2(5)	C(17)-C(18)	150.5(4)
C(1)-H(100)	97(3)	C(20)-N(2)	147.0(3)
C(1)-H(101)	97(3)	C(20)-C(21)	152.2(4)
C(12)-C(14)	140.9(4)	C(21)-N(3)	147.5(3)
C(12)-C(11)	141.2(4)	C(18)-N(2)	148.2(3)
C(12)-C(13)	143.2(4)	C(19)-N(2)	146.7(3)
C(12)-Li(2)	264.2(5)	C(15)-N(1)	147.2(3)

C(23)-N(3)	147.4(3)	C(2)-C(1)-H(100)	115.9(17)
C(22)-N(3)	147.1(3)	Li(1)-C(1)-H(100)	119.1(17)
C(16)-N(1)	146.6(3)	C(2)-C(1)-H(101)	115.0(17)
N(1)-Li(1)	216.3(5)	Li(1)-C(1)-H(101)	83.3(16)
N(2)-Li(1)	209.9(5)	H(100)-C(1)-H(101)	122(2)
N(3)-Li(1)	211.4(5)	C(14)-C(12)-C(11)	123.5(3)
N(6)-C(31)	146.3(4)	C(14)-C(12)-C(13)	122.5(3)
N(6)-C(32)	147.4(4)	C(11)-C(12)-C(13)	113.9(3)
N(6)-C(30)	147.6(3)	C(14)-C(12)-Li(2)	56.95(18)
N(6)-Li(2)	219.8(5)	C(11)-C(12)-Li(2)	87.32(18)
N(4)-C(26)	146.7(3)	C(13)-C(12)-Li(2)	127.8(2)
N(4)-C(24)	147.0(4)	C(10)-C(11)-C(12)	123.1(3)
N(4)-C(25)	148.3(4)	C(12)-C(14)-Li(2)	90.8(2)
N(4)-Li(2)	212.5(5)	C(12)-C(14)-H(103)	117.3(16)
N(5)-C(28)	146.4(3)	Li(2)-C(14)-H(103)	81.9(16)
N(5)-C(27)	147.2(3)	C(12)-C(14)-H(102)	116.0(17)
N(5)-C(29)	148.3(3)	Li(2)-C(14)-H(102)	122.2(17)
N(5)-Li(2)	210.0(5)	H(103)-C(14)-H(102)	120(2)
C(26)-C(27)	151.8(4)	C(11)-C(10)-C(9)	122.2(3)
C(29)-C(30)	150.4(4)	C(8)-C(13)-C(12)	121.9(3)
Li(2)-H(103)	229(3)	C(10)-C(9)-C(8)	118.1(3)
Li(1)-H(101)	230(3)	C(9)-C(8)-C(13)	120.8(3)
		N(1)-C(17)-C(18)	112.7(2)
C(7)-C(6)-C(5)	121.9(3)	N(2)-C(20)-C(21)	111.2(2)
C(1)-C(2)-C(7)	123.0(3)	N(3)-C(21)-C(20)	112.5(2)
C(1)-C(2)-C(3)	123.0(3)	N(2)-C(18)-C(17)	111.3(2)
C(7)-C(2)-C(3)	113.9(3)	C(16)-N(1)-C(15)	107.8(2)
C(1)-C(2)-Li(1)	54.67(18)	C(16)-N(1)-C(17)	110.9(2)
C(7)-C(2)-Li(1)	127.3(2)	C(15)-N(1)-C(17)	108.7(2)
C(3)-C(2)-Li(1)	89.94(19)	C(16)-N(1)-Li(1)	113.87(19)
C(3)-C(4)-C(5)	121.7(3)	C(15)-N(1)-Li(1)	115.6(2)
C(4)-C(5)-C(6)	117.3(3)	C(17)-N(1)-Li(1)	99.69(19)
C(6)-C(7)-C(2)	122.4(3)	C(19)-N(2)-C(20)	111.0(2)
C(4)-C(3)-C(2)	122.6(3)	C(19)-N(2)-C(18)	110.1(2)
C(2)-C(1)-Li(1)	93.9(2)	C(20)-N(2)-C(18)	111.9(2)

C(19)-N(2)-Li(1)	114.9(2)	N(4)-Li(2)-C(14)	123.4(2)
C(20)-N(2)-Li(1)	104.56(18)	N(6)-Li(2)-C(14)	115.5(2)
C(18)-N(2)-Li(1)	104.19(19)	N(5)-Li(2)-C(12)	143.6(2)
C(22)-N(3)-C(23)	108.4(2)	N(4)-Li(2)-C(12)	98.74(18)
C(22)-N(3)-C(21)	109.9(2)	N(6)-Li(2)-C(12)	122.01(19)
C(23)-N(3)-C(21)	110.5(2)	C(14)-Li(2)-C(12)	32.24(12)
C(22)-N(3)-Li(1)	119.4(2)	N(5)-Li(2)-H(103)	116.3(7)
C(23)-N(3)-Li(1)	105.8(2)	N(4)-Li(2)-H(103)	147.0(8)
C(21)-N(3)-Li(1)	102.55(19)	N(6)-Li(2)-H(103)	90.4(8)
C(31)-N(6)-C(32)	108.1(2)	C(14)-Li(2)-H(103)	25.3(7)
C(31)-N(6)-C(30)	110.6(2)	C(12)-Li(2)-H(103)	48.7(7)
C(32)-N(6)-C(30)	108.7(2)	N(2)-Li(1)-N(3)	87.29(18)
C(31)-N(6)-Li(2)	114.0(2)	N(2)-Li(1)-N(1)	87.32(18)
C(32)-N(6)-Li(2)	115.4(2)	N(3)-Li(1)-N(1)	114.7(2)
C(30)-N(6)-Li(2)	99.71(19)	N(2)-Li(1)-C(1)	116.1(2)
C(26)-N(4)-C(24)	110.4(2)	N(3)-Li(1)-C(1)	125.6(2)
C(26)-N(4)-C(25)	109.9(2)	N(1)-Li(1)-C(1)	114.8(2)
C(24)-N(4)-C(25)	108.7(2)	N(2)-Li(1)-C(2)	140.6(2)
C(26)-N(4)-Li(2)	103.79(19)	N(3)-Li(1)-C(2)	100.33(18)
C(24)-N(4)-Li(2)	117.9(2)	N(1)-Li(1)-C(2)	122.41(19)
C(25)-N(4)-Li(2)	105.9(2)	C(1)-Li(1)-C(2)	31.39(11)
C(28)-N(5)-C(27)	111.6(2)	N(2)-Li(1)-H(101)	116.5(7)
C(28)-N(5)-C(29)	110.0(2)	N(3)-Li(1)-H(101)	147.2(8)
C(27)-N(5)-C(29)	111.2(2)	N(1)-Li(1)-H(101)	90.0(8)
C(28)-N(5)-Li(2)	113.3(2)	C(1)-Li(1)-H(101)	24.8(7)
C(27)-N(5)-Li(2)	106.00(19)	C(2)-Li(1)-H(101)	46.9(7)
C(29)-N(5)-Li(2)	104.5(2)		
N(4)-C(26)-C(27)	112.2(2)		
N(5)-C(27)-C(26)	111.1(2)		
N(5)-C(29)-C(30)	111.1(2)		
N(6)-C(30)-C(29)	111.8(2)		
N(5)-Li(2)-N(4)	85.89(18)		
N(5)-Li(2)-N(6)	86.29(18)		
N(4)-Li(2)-N(6)	116.5(2)		
N(5)-Li(2)-C(14)	118.1(2)		

checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: final

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=7.6190(7) b=18.5142(16) c=9.8057(9)
alpha=90 beta=100.556(1) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	1359.8(2)	1359.8(2)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	?
Moiety formula	C18 H48 Li2 N2 O2 Si2	?
Sum formula	C18 H48 Li2 N2 O2 Si2	C18 H48 Li2 N2 O2 Si2
Mr	394.64	394.64
Dx,g cm-3	0.964	0.964
Z	2	2
Mu (mm-1)	0.142	0.142
F000	440.0	440.0
F000’	440.44	
h,k,lmax	9,24,12	9,24,12
Nref	3114	3113
Tmin,Tmax	0.983,0.993	0.972,0.993
Tmin’	0.972	

Correction method= MULTI-SCAN

Data completeness= 1.000 Theta(max)= 27.480

R(reflections)= 0.0332(2822) wR2(reflections)= 0.0893(3113)

S = 1.085 Npar= 132

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B
PLAT049_ALERT_1_B Calculated Density less than 1.0 gcm-3 ..... 0.96
PLAT230_ALERT_2_B Hirshfeld Test Diff for Si1 -- C3 .. 7.29 su

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Alert level C
PLAT303_ALERT_2_C Full Occupancy H-Atom H12 with # Connections 2

Alert level G

PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.14 Ratio

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0 **ALERT level A** = Most likely a serious problem - resolve or explain
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1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected

1 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
2 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Publication of your CIF in IUCr journals

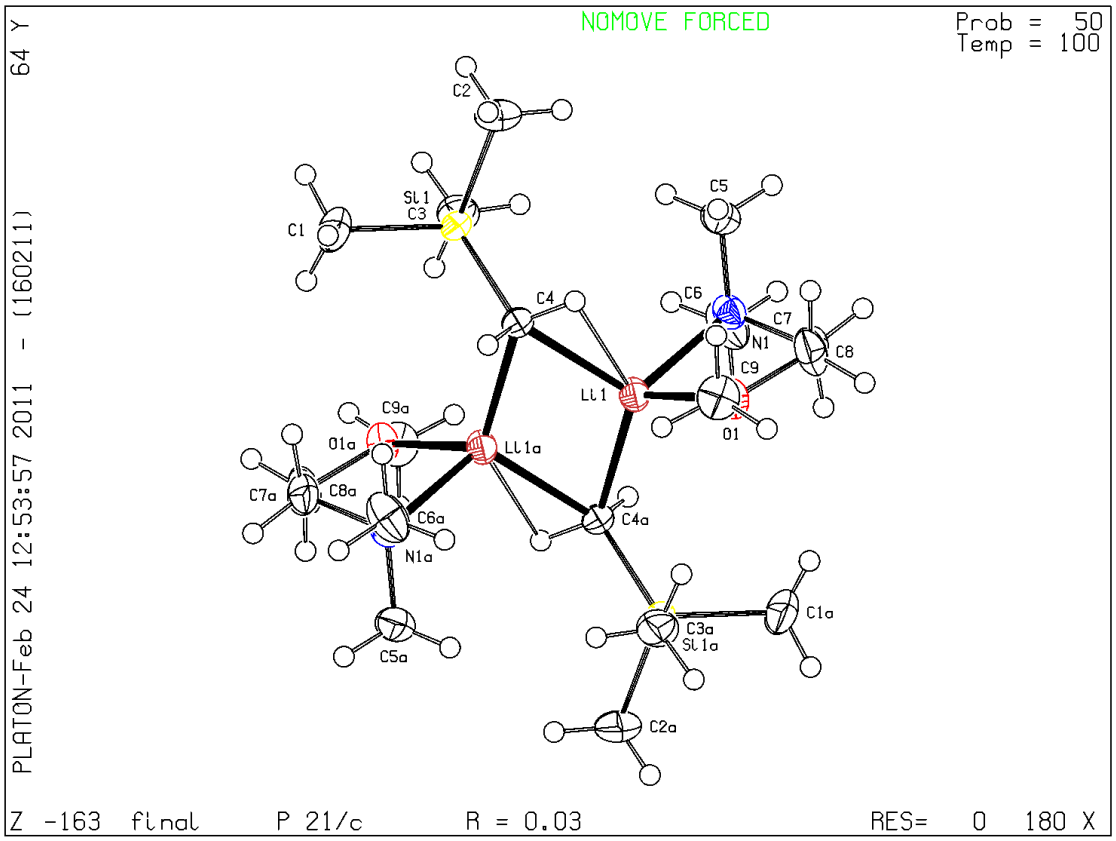
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 16/02/2011; check.def file version of 16/02/2011

Datablock final - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: finale

Bond precision: C-C = 0.0019 A Wavelength=0.71073

Cell: a=24.290(5) b=8.8900(18) c=24.520(5)
alpha=90 beta=111.23(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	4936(2)	4935.5(17)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C48 H80 Li4 N4 O4	?
Sum formula	C48 H80 Li4 N4 O4	C48 H80 Li4 N4 O4
Mr	804.92	804.92
Dx,g cm-3	1.083	1.083
Z	4	4
Mu (mm-1)	0.066	0.066
F000	1760.0	1760.0
F000’	1760.62	
h,k,lmax	34,12,34	34,12,34
Nref	7165	6888
Tmin,Tmax	0.992,0.993	0.980,0.993
Tmin’	0.980	

Correction method= MULTI-SCAN

Data completeness= 0.961 Theta(max)= 29.930

R(reflections)= 0.0452(5605) wR2(reflections)= 0.1281(6888)

S = 1.058 Npar= 342

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

CELLV02_ALERT_1_C The supplied cell volume s.u. differs from that
calculated from the cell parameter s.u.’s by > 2
Calculated cell volume su = 20.13
Cell volume su given = 17.00
PLAT152_ALERT_1_C The Supplied and Calc. Volume s.u. Differ by ... 3 Units
PLAT220_ALERT_2_C Large Non-Solvent C Ueq(max)/Ueq(min) ... 3.05 Ratio

```
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for         N1
PLAT701_ALERT_1_C Bond    Calc  1.4673(16), Rep  1.4692(15), Dev..       1.19 Sigma
              N2   -C15     1.555   1.555                    #         45
PLAT701_ALERT_1_C Bond    Calc  1.4279(16), Rep  1.4298(15), Dev..       1.19 Sigma
              O2   -C19     1.555   1.555                    #         54
PLAT701_ALERT_1_C Bond    Calc  1.5069(17), Rep  1.5089(17), Dev..       1.18 Sigma
              C17  -C18     1.555   1.555                    #         55
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Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         18
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites ....         34
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 =          3
PLAT301_ALERT_3_G Note: Main Residue  Disorder ...................         13 Perc.
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) .       1.13 Ratio
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        147
              C22' -N1   -C22     1.555   1.555   1.555              7.30 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        160
              H20B -C20  -H20D    1.555   1.555   1.555              7.10 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        165
              H20C -C20  -H20E    1.555   1.555   1.555              7.10 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        168
              H20A -C20  -H20F    1.555   1.555   1.555              7.10 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        181
              H21B -C21  -H21D    1.555   1.555   1.555              0.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        186
              H21C -C21  -H21E    1.555   1.555   1.555              0.60 Deg.
PLAT779_ALERT_4_G Suspect or Irrelevant (Bond) Angle in CIF .... #        189
              H21A -C21  -H21F    1.555   1.555   1.555              0.60 Deg.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......        175
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```

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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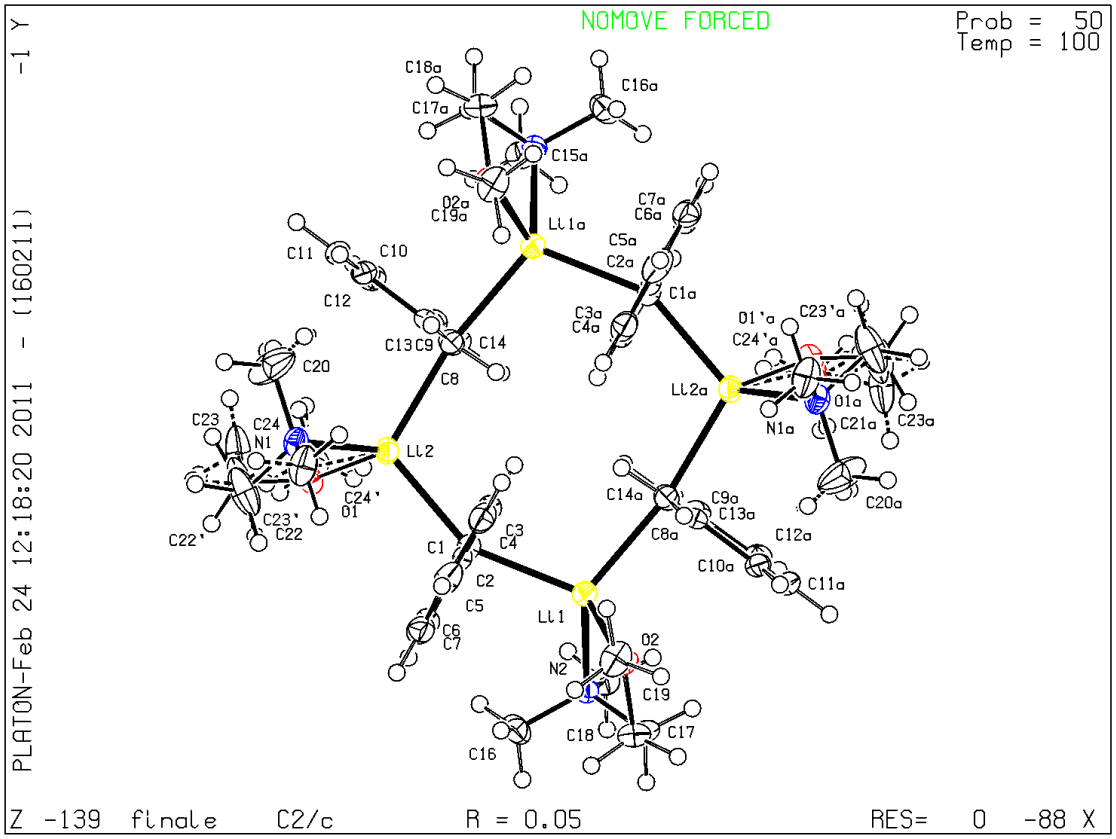
PLATON version of 16/02/2011; check.def file version of 16/02/2011

Datablock finale - ellipsoid plot



checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: sad2

Bond precision: C-C = 0.0042 A Wavelength=0.71073

Cell: **a=15.388(10)** **b=13.379(8)** **c=17.068(11)**
alpha=90 **beta=93.381(11)** **gamma=90**
Temperature: **100 K**

	Calculated	Reported
Volume	3508(4)	3508(4)
Space group	P 21/c	P21/c
Hall group	-P 2ybc	?
Moiety formula	C16 H30 Li N3	?
Sum formula	C16 H30 Li N3	C16 H30 Li N3
Mr	271.37	271.37
Dx,g cm-3	1.028	1.028
Z	8	8
Mu (mm-1)	0.060	0.060
F000	1200.0	1200.0
F000'	1200.32	
h,k,lmax	15,13,17	15,13,17
Nref	4093	4068
Tmin,Tmax	0.993,0.995	0.982,0.995
Tmin'	0.982	

Correction method= MULTI-SCAN

Data completeness= 0.994 **Theta(max)= 21.650**

R(reflections)= 0.0500(3146) **wR2(reflections)= 0.1298(4068)**

S = 1.078 **Npar= 387**

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A
THETM01_ALERT_3_A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.5191

Alert level G
PLAT793_ALERT_4_G The Model has Chirality at N2 (Verify) .... R

PLAT793_ALERT_4_G The Model has Chirality at N5 (Verify) .... R

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PLATON version of 16/02/2011; check.def file version of 16/02/2011

Datablock sad2 - ellipsoid plot