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Supporting Information (7 pages)

"A Likely Intermediate During the CO_2-induced Activation of 2-Alkylindoles Towards Electrophilic Substitution: Structure of a Unique Tetramer Formed by Joining Two Boat-shaped $(LiOCO)_2$ Rings"

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Synthesis and Characterisation of the title compound, $(2 \cdot thf)_n$.

A solution of 2,3-dimethylindole, **1** (0.725g, 5.0 mmol) in dry thf (8ml) was chilled in a dry ice / acetone bath. A hexane solution of n-butyl lithium (3.2ml of a 1.6 mol dm^{-3} solution, 5.0 mmol) was added with stirring, and the mixture warmed to room temperature to give a clear dark orange solution. The solution was treated with gaseous CO_2 resulting in a pale yellow solution. Partial removal of solvent (to 5 ml) and refrigeration at 5 °C for 2 days afforded pale yellow cubic crystals identified as $(2 \cdot thf)_n$.

Yield (first batch): 0.890g, 67%
M.P. > 320 °C

Analyses : $C_{15}H_{18}LiNO_3$	requires	C 67.42; H 6.74; N 5.24 %
	found	C 66.82; H 6.81; N 5.25 %

^1H NMR (250 MHz, d8-thf, 25 °C): δ 8.36-6.90 (m, 4H, Ar*H*), 3.57 (m, 4H, *thf*), 2.54 (s, 3H, *Me*), 2.13 (s, 3H, *Me*), 1.77 (m, 4H, *thf*).

On subsequent pages:

Table 1. Crystal data and structure refinement

Identification code	sich10
Empirical formula	$C_{60}H_{72}Li_4N_4O_{12}$
Formula weight	1068.98
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	$I4_1/a$
Unit cell dimensions	a = 16.288(4) Å α = 90° b = 16.288(4) Å β = 90° c = 21.674(6) Å γ = 90°
Volume	5750(3) $Å^3$
Z	4
Density (calculated)	1.235 Mg/m^3
Absorption coefficient	0.084 mm^{-1}
F(000)	2272
Crystal size	0.45 x 0.45 x 0.45 mm
θ range for data collection	3.54 to 25.00°
Index ranges	$-1 \leq h \leq 19$, $-19 \leq k \leq 19$, $-25 \leq \ell \leq 25$
Reflections collected	3277
Independent reflections	2527 (R_{int} = 0.0158)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2526 / 0 / 201
Goodness-of-fit on F^2	1.036
Final R indices [I>2σ(I)]	R1 = 0.0449, wR2 = 0.1053
R indices (all data)	R1 = 0.0620, wR2 = 0.1216
Largest diff. peak and hole	0.189 and -0.236 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
N(1)	1215(1)	2006(1)	-275(1)	29(1)
C(1)	927(1)	1748(1)	-863(1)	33(1)
C(2)	1480(1)	1972(1)	-1299(1)	39(1)
C(3)	2155(1)	2362(1)	-996(1)	37(1)
C(4)	1981(1)	2391(1)	-358(1)	31(1)
C(5)	2905(1)	2677(1)	-1209(1)	48(1)
C(6)	3448(1)	3002(1)	-796(1)	51(1)
C(7)	3264(1)	3027(1)	-166(1)	48(1)
C(8)	2530(1)	2722(1)	64(1)	37(1)
C(9)	800(1)	1906(1)	297(1)	27(1)
O(1)	234(1)	1398(1)	314(1)	35(1)
O(2)	1050(1)	2341(1)	742(1)	30(1)
C(10)	123(1)	1326(1)	-955(1)	43(1)
C(11)	1417(2)	1857(2)	-1989(1)	59(1)
Li(1)	-605(2)	1543(2)	918(1)	30(1)
O(3)	-1410(1)	699(1)	855(1)	44(1)
C(12)	-1869(2)	400(2)	1360(1)	60(1)
C(13)	-2682(2)	184(3)	1098(1)	83(1)
C(14)	-2503(2)	-83(2)	447(1)	52(1)
C(15)	-1673(1)	293(1)	304(1)	40(1)

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

N(1)-C(4)	1.408(2)	N(1)-C(1)	1.422(2)
N(1)-C(9)	1.421(2)	C(1)-C(2)	1.355(3)
C(1)-C(10)	1.492(3)	C(2)-C(3)	1.430(3)
C(2)-C(11)	1.510(3)	C(3)-C(5)	1.403(3)
C(3)-C(4)	1.413(3)	C(4)-C(8)	1.388(3)
C(5)-C(6)	1.365(3)	C(6)-C(7)	1.399(3)
C(7)-C(8)	1.388(3)	C(9)-O(1)	1.240(2)
C(9)-O(2)	1.264(2)	C(9)-Li(1)	2.721(4) ?
O(1)-Li(1)	1.908(3)	O(2)-Li(1b)	1.966(3)
O(2)-Li(1a)	1.993(3)	Li(1)-O(3)	1.905(3)
Li(1)-O(2b)	1.966(3)	Li(1)-O(2a)	1.993(3)
Li(1)-Li(1a)	2.978(5)	Li(1)-Li(1b)	2.978(5)
O(3)-C(12)	1.413(2)	O(3)-C(15)	1.430(2)
C(12)-C(13)	1.484(4)	C(13)-C(14)	1.506(4)
C(14)-C(15)	1.516(3)		

C(4)-N(1)-C(1)	108.0(2)	C(4)-N(1)-C(9)	125.8(2)
C(1)-N(1)-C(9)	126.2(2)	C(2)-C(1)-N(1)	109.1(2)
C(2)-C(1)-C(10)	127.9(2)	N(1)-C(1)-C(10)	123.0(2)
C(1)-C(2)-C(3)	108.0(2)	C(1)-C(2)-C(11)	127.8(2)
C(3)-C(2)-C(11)	124.2(2)	C(5)-C(3)-C(4)	119.0(2)
C(5)-C(3)-C(2)	132.9(2)	C(4)-C(3)-C(2)	108.1(2)
C(8)-C(4)-N(1)	131.3(2)	C(8)-C(4)-C(3)	122.0(2)
N(1)-C(4)-C(3)	106.7(2)	C(6)-C(5)-C(3)	119.4(2)
C(5)-C(6)-C(7)	120.8(2)	C(8)-C(7)-C(6)	121.6(2)
C(7)-C(8)-C(4)	117.2(2)	O(1)-C(9)-O(2)	126.2(2)
O(1)-C(9)-N(1)	117.2(2)	O(2)-C(9)-N(1)	116.6(2)
? O(1)-C(9)-Li(1)	38.22(10)	O(2)-C(9)-Li(1)	90.83(12) ?
N(1)-C(9)-Li(1)	148.98(14)	C(9)-O(1)-Li(1)	118.07(14)
C(9)-O(2)-Li(1b)	118.3(2)	C(9)-O(2)-Li(1a)	122.70(14)
Li(1a)-O(2)-Li(1b)	97.58(13)	O(3)-Li(1)-O(1)	110.7(2)
O(3)-Li(1)-O(2b)	105.4(2)	O(1)-Li(1)-O(2b)	111.2(2)
O(3)-Li(1)-O(2a)	113.3(2)	O(1)-Li(1)-O(2a)	104.0(2)
O(2b)-Li(1)-O(2a)	112.5(2)	O(3)-Li(1)-C(9)	134.4(2)
O(1)-Li(1)-C(9)	23.71(7)	O(2b)-Li(1)-C(9)	99.44(13)
O(2a)-Li(1)-C(9)	90.71(12)	O(3)-Li(1)-Li(1b)	121.3(2)
O(1)-Li(1)-Li(1b)	125.11(13)	O(2b)-Li(1)-Li(1b)	71.92(12)
O(2a)-Li(1)-Li(1b)	40.87(8)	C(9)-Li(1)-Li(1a)	102.42(9)
O(3)-Li(1)-Li(1c)	139.6(2)	O(1)-Li(1)-Li(1c)	75.13(12)
O(2a)-Li(1)-Li(1c)	41.56(11)	O(2b)-Li(1)-Li(1c)	103.15(9)
C(9)-Li(1)-Li(1c)	58.57(9)	Li(1b)-Li(1)-Li(1c)	76.52(9)
C(12)-O(3)-C(15)	109.2(2)	C(12)-O(3)-Li(1)	123.8(2)
C(15)-O(3)-Li(1)	126.9(2)	O(3)-C(12)-C(13)	104.9(2)
C(12)-C(13)-C(14)	104.8(2)	C(13)-C(14)-C(15)	104.3(2)
O(3)-C(15)-C(14)	106.5(2)		

Symmetry transformations used to generate equivalent atoms:

c -y+1/4,x+1/4,-z+1/4 a -x+1-1,-y+1/2,z+1-1 b y-1/4,-x+1/4,-z+1/4

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$]

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
N(1)	36(1)	32(1)	19(1)	0(1)	4(1)	3(1)
C(1)	47(1)	33(1)	20(1)	-4(1)	1(1)	7(1)
C(2)	63(1)	34(1)	21(1)	1(1)	10(1)	10(1)
C(3)	52(1)	28(1)	33(1)	5(1)	17(1)	11(1)
C(4)	35(1)	27(1)	30(1)	3(1)	9(1)	6(1)
C(5)	58(1)	39(1)	46(1)	10(1)	27(1)	11(1)
C(6)	43(1)	42(1)	68(2)	14(1)	24(1)	4(1)
C(7)	36(1)	44(1)	63(2)	9(1)	5(1)	2(1)
C(8)	35(1)	39(1)	38(1)	3(1)	5(1)	4(1)
C(9)	30(1)	31(1)	20(1)	-1(1)	3(1)	8(1)
O(1)	38(1)	41(1)	26(1)	-6(1)	8(1)	-7(1)
O(2)	35(1)	36(1)	18(1)	-2(1)	1(1)	2(1)
C(10)	54(1)	49(1)	27(1)	-9(1)	-5(1)	2(1)
C(11)	99(2)	56(2)	23(1)	-1(1)	14(1)	8(2)
Li(1)	34(2)	34(2)	22(1)	0(1)	-1(1)	-4(1)
O(3)	56(1)	50(1)	26(1)	-7(1)	5(1)	-24(1)
C(12)	63(2)	83(2)	35(1)	-3(1)	12(1)	-39(2)
C(13)	56(2)	129(3)	64(2)	-25(2)	14(1)	-40(2)
C(14)	54(1)	44(1)	58(2)	-6(1)	-15(1)	-9(1)
C(15)	52(1)	39(1)	31(1)	-9(1)	-7(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3)

	x	y	z	U(eq)
H(5A)	3031(1)	2665(1)	-1642(1)	60(7)
H(6A)	3966(1)	3210(1)	-939(1)	71(8)
H(7A)	3654(1)	3266(1)	114(1)	59(7)
H(8A)	2404(1)	2738(1)	497(1)	42(6)
H(10A)	144(3)	779(4)	-767(6)	63(7)
H(10B)	12(4)	1273(8)	-1397(1)	61(7)
H(10C)	-314(2)	1648(5)	-760(6)	60(7)
H(11A)	981(9)	1460(10)	-2082(1)	112(13)
H(11B)	1941(4)	1652(12)	-2149(2)	105(12)
H(11C)	1287(13)	2384(3)	-2184(1)	101(11)
H(12A)	-1921(2)	809(2)	1677(1)	77(9)
H(12B)	-1608(2)	-77(2)	1531(1)	163(19)
H(13A)	-3040(2)	652(3)	1106(1)	172(22)
H(13B)	-2933(2)	-255(3)	1325(1)	111(12)
H(14A)	-2917(2)	121(2)	171(1)	80(9)
H(14B)	-2482(2)	-670(2)	414(1)	73(8)
H(15A)	-1287(1)	-125(1)	188(1)	59(7)
H(15B)	-1719(1)	680(1)	-28(1)	49(6)