Oxygen Capture by Lithiated Organozinc Reagents Containing Aromatic 2-Pyridylamide Ligands

Robert P. Davies,[b] David J. Linton,[a] Paul Schooler,[a] Ronald Snaith,[a] and Andrew E. H. Wheatley*[a]

Abstract: The sequential reaction of $\mathrm{ZnMe_2}$ with a 2-pyridylamine ($\mathrm{HN(2\text{-}C_5H_4N)R}$, R = Ph: **1**; 3,5-Xy (= 3,5-xylyl): **2**; 2,6-Xy: **3**; Bz (= benzyl): **4**; Me: **5**), *t*BuLi and thereafter with oxygen affords various lithium zincate species, the solid-state structures of which reveal a diversity of oxo-capture modes. Amine **1** reacts to give both dimeric $\mathrm{THF\cdot[Li(Me)OZn\{N(2\text{-}C_5H_4N)Ph\}_2]}$ (**6**), wherein oxygen has inserted into the Zn–C bond of a $\mathrm{\{MeZn[N(2\text{-}C_5H_4N)Ph]_2\}^-}$ ion, and the trigonal $\mathrm{Li_2Zn}$ complex, *bis*(O*t*Bu)-capped $\mathrm{(THF\cdot Li)_2[\{(\mu_3\text{-}O)\mathit{t}Bu\}_2Zn\{N(2\text{-}C_5H_4N)Ph\}_2]}$ (**7**). The structural analogue of **6** (**8**) results from the employment of **2**, while the use of more sterically congested **3** yields a pseudo-cubane dimer $\mathrm{[\{THF\cdot[Li(\mathit{t}Bu)OZn(O\mathit{t}Bu)Me]\}_2]}$ (**9**) notable for the retention of labile Zn–C(Me). Amines **4** and **5** afford the oxo-encapsulation products $\mathrm{[(\mu_4\text{-}O)Zn_4\{(2\text{-}C_5H_4N)NBz\}_6]}$ (**10b**), and $\mathrm{[\mathit{t}Bu(\mu_3\text{-}O)Li_3(\mu_6\text{-}O)Zn_3\{(2\text{-}C_5H_4N)NMe\}_6]}$ (**11**), respectively, with concomitant oxo-insertion into a Li–C interaction resulting in capping of the *fac*-isomeric $\mathrm{(\mu_6\text{-}O)M_3M'_3}$ distorted octahedral core of the latter complex by a *tert*-butoxide group.

Keywords: lithium · oxygen capture · solid-state structures · zinc

Introduction

Much of the current interest in correlating the chemical and structural properties of lithium-containing heterobimetallic species derives from their ability to effect organic transformations whose selectivity differs from that of the parent organolithium species.[1] The field of mixed Li–Zn chemistry furnishes several such examples. Hence, triorganozincate salts of lithium have been treated with propargylic species[2] to give intermediate allenic zinc complexes and thence α-,γ-disubstituted propargyles or allenes,[3] with aryl halides[4] to promote halogen–zinc exchange, with 1,1-dihalocyclopropyls[5] and 1-haloalkenylzincates[6] to afford metal carbenoids,[7] and with either 1,1-dihaloalkenes[8] or 1-haloalkyls[9] to give polyfunctionalized products. The solution structures of ligand–reagent complexes[10] which effect the stereoselective alkylation of carbonyl groups[11] have lately been probed. Moreover, while organolithium reagents have been found to add 1,2 across α,β-unsaturated ketones,[12] certain lithium silyl(dialkyl)zincates have been found to effect conjugate addition instead.[13] More recently, the dilithium tetraorganozincate species $\mathrm{Li_2ZnMe_3R}$ (R = Me, CN, SCN) have been developed.[14] While these salts, with their essentially tetrahedral dianions,[15] have long been known,[16] their synthetic potential has only recently been realised.[14, 17]

In spite of the many uses of lithium organozincates, the structural chemistry of these species is not well understood. While the first solid-state characterisation of a mixed Li–Zn compound was of the straightforwardly ion-separated bis(lithium) tetraalkylzincate $\mathrm{(Li^+)_2\,ZnMe_4{}^-}$,[18] ion-separated homoleptic triorganozincates ($\mathrm{Li^+\,ZnR_3{}^-}$) have proved to be more common. Mixed coordination of the Group 1 metal centre has been observed in $\mathrm{[Li(Et_2O)(TMEDA)]^+[Zn\{C(H)(SiMe_3)_2\}_3]^-}$,[19] while bis(TMEDA) chelation (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) of the $\mathrm{Li^+}$ ion is recorded in the salts of the heteroleptic zincates $\mathrm{[Zn(Me)_2C(H)(Ph)SiMe_3]^-}$ and $\mathrm{[Zn(Me)\{C(H)(Ph)SiMe_3\}_2]^-}$,[20] and two equivalents of 1,3,5-trimethyl-1,3,5-triazine (L) envelop the $\mathrm{Li^+}$ ion in $\mathrm{[Li(L)_2]^+[Zn(Me)\{C(H)[Si(Me)_2C(H)_2]_2SiMe_2\}_2]^-}$.[21] The inclusion of electron-rich heteroatoms in the zinc-bonded organic residues has afforded ion-associated species. For example, $\mathrm{L\cdot[LiZn(CH_2SiMe_3)_2N(SiMe_3)_2]}$ displays a Li(μ-N)Zn bridge.[21] Such monobridged motifs are also possible in the absence of a heteroatom, and in fact Li(μ-C)Zn and

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Li(μ-C)$_2$Zn motifs dominate the known structures of ion-bonded lithium zincates. Monomeric THF·[LiZn{2-(NMe$_2$CH$_2$)C$_6$H$_4$}$_3$] reveals a mono-aryl bridge between metal centres,[22] while double bridging is synonymous with tetra- rather than triorganozincate salts. Hence, spirocyclic Li(μ-C)$_2$Zn(μ-C)$_2$Li arrangements define the structures of L·[Li$_2$Zn{(CH$_2$)$_4$}$_2$],[23] L·[Li$_2$Zn(C≡CPh)$_4$],[24] L·[Li$_2$Zn{(CH$_2$SiMe$_2$)$_2$}$_2$],[25] (L = TMEDA) and also [Li$_2$Zn{2-(NMe$_2$CH$_2$)C$_6$H$_4$}$_4$][22] and polymeric [Li$_2$Zn{O$_2$C(CH)$_2$Me}$_4$].[26]

In the light of advances in the controlled oxygenation of lithium-[27] and potassium-containing[28] mixed s-block metal compounds and, more recently, lithium aluminates,[29] we report here the incorporation of oxygen into mixed lithium-zinc systems and detail the structural characterisations of several new mixed Li–Zn species. Specifically, we discuss the variability and selectivity of oxo-capture revealed on treatment with air (pre-dried over P$_2$O$_5$)[29] of the Li–Zn systems which result from the reaction of ZnMe$_2$ with 2-pyridylamines (HN(2-C$_5$H$_4$N)R, R = Ph: **1**; 3,5-Xy (= 3,5-xylyl): **2**; 2,6-Xy: **3**; Bz (= benzyl): **4**; Me: **5**) and thereafter with *t*BuLi (Scheme 1).

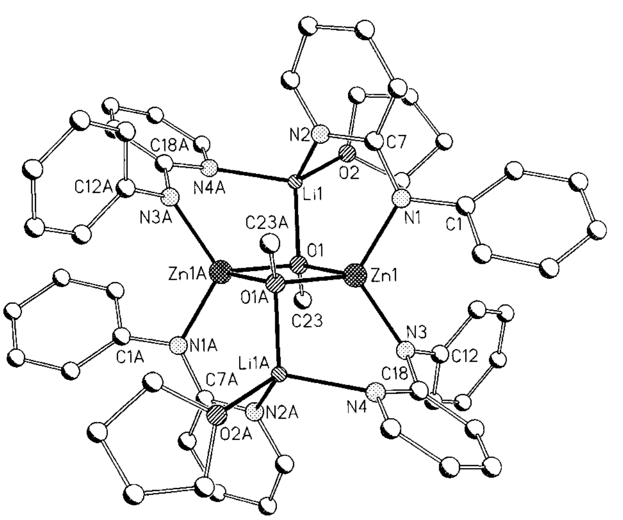


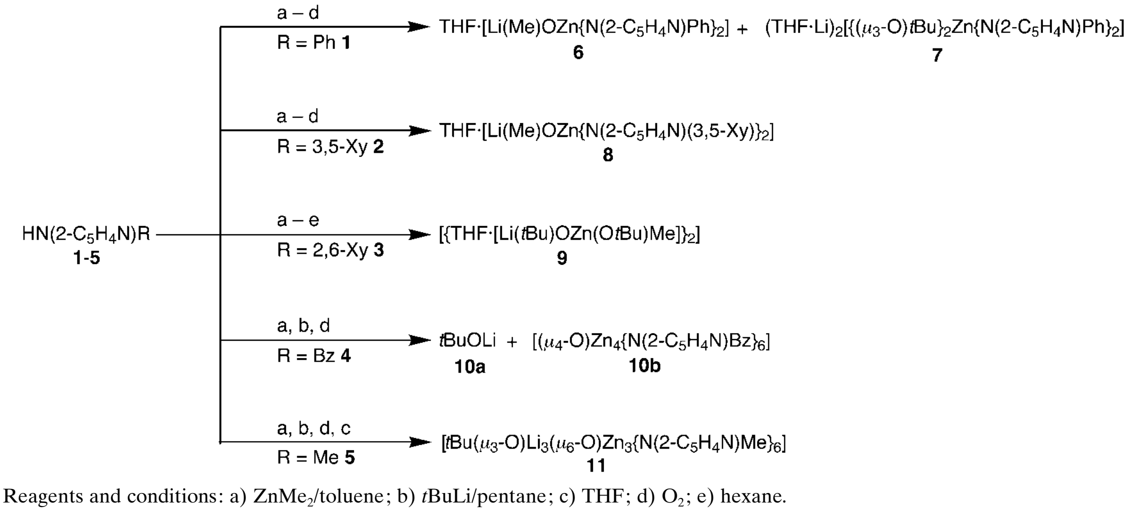
Figure 1. Molecular structure of dimeric **6**; hydrogen atoms and lattice THF molecule omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for dimeric **6**.

Li1–O1	1.915(7)	Zn1–N3	1.976(3)
Li1–O2	1.936(6)	O1–C23	1.432(5)
Li1–N2	2.077(7)	N1–C7	1.353(6)
Li1–N4A	2.064(7)	N2–C7	1.371(5)
Zn1–O1	2.001(3)	N3–C18	1.353(5)
Zn1–O1A	2.031(2)	N4–C18	1.368(5)
Zn1–N1	1.980(3)		
Li1-O1-C23	116.1(3)	O1-Zn1-N1	115.01(13)
Li1-O1-Zn1	104.9(2)	O1-Zn1-N3	111.11(12)
Li1-N2-C7	127.8(3)	Zn1-N1-C7	123.6(3)
Li1-N4A-C18A	120.8(3)	Zn1-N3-C18	120.3(3)
O1-Li1-O2	117.0(4)	N1-C7-N2	117.2(4)
O1-Li1-N2	108.1(3)	N3-C18-N4	115.8(4)
O1-Li1-N4A	103.9(3)		

Results and Discussion

Reaction of a non-donor solution of (2-C$_5$H$_4$N)N(H)R (R = Ph **1**) with ZnMe$_2$ results in deprotonation and the facile evolution of CH$_4$. Thereafter, sequential treatment of the system with *t*BuLi and with air (pre-dried over P$_2$O$_5$) until the evolution of fumes subsided afforded a slurry which dissolved on addition of Lewis base. At ambient temperature the solution yields two crystalline materials, **6** and **7**, which can be mechanically separated. X-ray crystallography reveals **6** to be a dimer in the solid state (Figure 1, Table 1), the halves of which are symmetry-related—the asymmetric unit containing half of the dimer and a whole lattice THF molecule. The structure is built around a planar (ZnO)$_2$ ring (mean Zn–O 2.016 Å; O-Zn-O 85.6(1), Zn-O-Zn 94.4(1)°) the formation of which renders each zinc centre tetrahedral and implies oxo-insertion into the Zn–C bond of a lithium triorganozincate unit.[30] The alkali metal centres are *anti*-disposed about the (ZnO)$_2$ heterocycle, lying exocyclic to it and interacting with the core O centres (Li1–O1 1.915(7) Å). Each Li$^+$ centre is electronically augmented by the coordination of two pyridyl N centres (mean Li–N 2.071 Å). Since these two aromatic systems are components of ligands which are themselves bonded to one



Scheme 1. Reagents and conditions: a) ZnMe$_2$/toluene; b) *t*BuLi/pentane; c) THF; d) O$_2$; e) hexane.

Zn centre each the result is the formation of a contiguous (LiO-edge-fused) pair of M-O-M′-N-C-N six-membered rings in each of which an N-C-N fragment spans a Li-O-Zn moiety.

The observation that, in spite of the reaction stoichiometry, **6** incorporates two equivalents of pyridylamide ligand per zinc centre suggests a complex reaction mechanism involving the formation of by-products. Weight is given to this view by the observation of a trace aliphatic signal at $\delta = 1.17$ in the ^1H NMR spectrum of the product. Indeed, it transpires that the synthesis of **6** is concomitant with that of **7**, the solid-state structure of which reveals a non-bonded triangular Li_2Zn core (Li ⋯ Li 2.635(6) Å, mean Li ⋯ Zn 2.607 Å; Figure 2, Table 2).

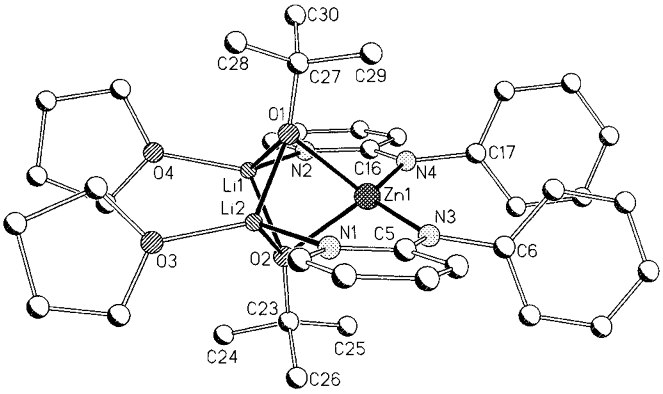


Figure 2. Molecular structure of Li_2Zn-based **7**; hydrogen atoms and minor O*t*Bu and THF disorder omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for Li_2Zn-based trigonal **7**.

Zn1–O1	2.0149(16)	Li2–O2	1.948(5)
Zn1–O2	2.0173(16)	Li2–O3	1.965(5)
Zn1–N3	1.979(2)	Li2–N1	2.058(5)
Zn1–N4	1.983(2)	N1–C5	1.361(4)
Li1–O1	1.941(4)	N2–C16	1.359(3)
Li1–O2	1.953(4)	N3–C5	1.356(3)
Li1–O4	1.960(5)	N3–C6	1.430(4)
Li1–N2	2.057(4)	N4–C16	1.353(3)
Li2–O1	1.954(4)	N4–C17	1.433(3)
Li1-O1-Li2	85.17(19)	O1-Li1-N2	112.1(2)
Li1-O1-C27	132.52(19)	O1-Li2-O2	80.84(17)
Li1-O2-C23	132.63(19)	O1-Li2-N1	104.6(2)
Li1-O1-Zn1	82.25(14)	O1-Zn1-O2	77.71(7)
Li1-O2-Li2	85.01(19)	O1-Zn1-N3	114.04(8)
Li1-O2-Zn1	81.89(13)	O1-Zn1-N4	110.58(8)
Li1-N2-C16	126.48(19)	Zn1-O1-C27	123.55(15)
Li2-O1-C27	132.80(19)	Zn1-O2-C23	123.23(16)
Li2-O2-C23	133.20(19)	Zn1-N3-C5	122.69(19)
Li2-O1-Zn1	82.28(15)	Zn1-N4-C16	123.13(18)
Li2-O2-Zn1	82.38(14)	N1-C5-N3	117.6(2)
Li2-N1-C5	126.7(2)	N2-C16-N4	117.5(2)
O1-Li1-O2	81.04(16)		

The integrity of this arrangement is retained for two reasons. The first is spanning of each heterobimetallic edge of the core by 2-pyridylamide ligands, rendering the zinc centre formally divalent (mean Zn–N 1.981 Å) with the pyridyl N centres stabilising the Li^+ ions (mean Li–N 2.058 Å). The second phenomenon which facilitates retention of the core is biscapping of the bimetallic motif by in-situ-generated O*t*Bu⁻ fragments. While this implies direct oxygenation of *t*BuLi (and explains the observation of an aliphatic contaminant in the ^1H NMR spectrum of **7**), it is worth noting that in spite of the known tendency for organolithium species to react with oxygen to afford peroxides in the first instance,[31] the O1 ⋯ O2 distance (2.530(2) Å) is incompatible with the presence of bis(*tert*-butyl)peroxide in the structure of **7**. The alkoxy groups reside significantly closer to the alkali metal centres than to the zinc centre (mean Li–O*t*Bu 1.949 Å, mean Zn–O*t*Bu 2.016 Å) and deviate noticeably from the normal to the Li_2Zn triangular core (mean smallest C-O-(Li_2Zn plane) 84.4°). This inclination of the O*t*Bu group goes some way towards increasing the effectiveness with which a filled O-centred sp^3 orbital is orientated towards Zn1 (mean Zn1-O-C(*t*Bu) 123.39°). However, it concomitantly depletes the interaction of the remaining, filled sp^3 orbitals on oxygen with each alkali metal ion to some extent and this is reflected in the large (mean) Li-O-C(*t*Bu) angle of 132.79°.[32] The inclination of the *tert*-butoxy fragments with respect to the isosceles Li_2Zn arrangement effectively amounts to a distortion of LiO*t*Bu in order to electrostatically satisfy an otherwise divalent zinc centre. Thus, in spite of the relatively long Li–O*t*Bu interactions,[32] **7** is perhaps best viewed as a 2:1 LiO*t*Bu:Zn{N(2-C_5H_4N)Ph}$_2$ adduct rather than as a dilithium tetraorganozincate. This conclusion also seems to be reasonable bearing in mind the relative sources of Me (in **6**) and *t*Bu (in **7**) groups.

Reaction of (2-C_5H_4N)N(H)(3,5-Xy) (**2**) with $ZnMe_2$, followed by treatment with *t*BuLi and with air (P_2O_5), afforded a suspension which dissolved on treatment with THF. The resultant solution deposited crystals which were shown by crystallography to be **8**, a solid-state dimer (one half of which is symmetry-related to the other and for whose formulation there exists one molecule of toluene in the lattice) which is an oxygenated lithium triorganozincate structurally analogous to **6** (Figure 3, Table 3). The planar $(ZnO)_2$ ring at the core of dimeric **8** (mean Zn–O 2.0222 Å; O-Zn-O 85.28(7)°, Zn-O-Zn 94.72(7)°) is extremely similar to that noted for the 2-pyridylanilide complex. The alkali metal

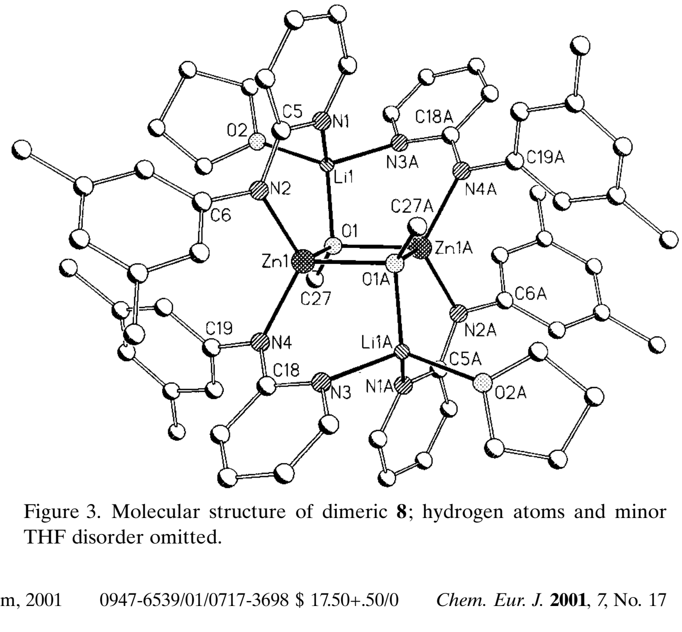


Figure 3. Molecular structure of dimeric **8**; hydrogen atoms and minor THF disorder omitted.

Table 3. Selected bond lengths [Å] and angles [°] for dimeric **8**.

Li1–O1	1.897(5)	Zn1–N4	1.980(2)
Li1–O2	1.976(5)	O1–C27	1.431(3)
Li1–N1	2.070(5)	N1–C5	1.357(3)
Li1–N3A	2.070(5)	N2–C5	1.365(3)
Zn1–O1	2.0129(16)	N3–C18	1.361(3)
Zn1–O1A	2.0314(16)	N4–C18	1.343(3)
Zn1–N2	1.975(2)		
Li1-O1-C27	114.7(2)	O1-Zn1-N2	111.34(8)
Li1-O1-Zn1	105.07(15)	O1-Zn1-N4	108.65(7)
Li1-N1-C5	129.1(2)	Zn1-N2-C5	122.73(16)
Li1-N3A-C18A	118.1(2)	Zn1-N4-C18	121.64(16)
O1-Li1-O2	114.9(2)	N1-C5-N2	116.4(2)
O1-Li1-N1	107.6(2)	N3-C18-N4	116.2(2)
O1-Li1-N3A	105.8(2)		

centres, again *anti*-disposed about the $(ZnO)_2$ heterocycle, interact more closely with the core O centres than in the analogous dimer (Li1–O1 1.897(5) Å, cf. Li1–O1 1.915(7) Å in **6**). In spite of this, the observed coordination of each Li^+ ion by two pyridyl N centres is unchanged (mean Li–N 2.070 Å) and again results in the formation of a contiguous (LiO-edge-fused) pair of six-membered rings.

Table 4. Selected bond lengths [Å] and angles [°] for dimeric pseudo-cubane **9**.

Li2–O2	2.011(6)	Li1–O1	2.008(6)
Li2–O3	1.957(7)	Li1–O3	1.976(6)
Li2–O4	1.977(7)	Li1–O4	1.982(7)
Li2–O6	2.039(7)	Li1–O5	2.060(6)
Zn2–O1	2.057(3)	Zn1–O1	2.060(2)
Zn2–O2	2.063(3)	Zn1–O2	2.070(3)
Zn2–O4	2.022(3)	Zn1–O3	2.011(2)
Zn2–C18	1.974(4)	Zn1–C17	1.988(4)
O2–C5	1.438(4)	O1–C1	1.439(4)
O3–C9	1.416(5)	O4–C13	1.427(5)
Li1-O1-C1	130.0(3)	Li2-O2-Zn1	88.4(2)
Li1-O3-C9	127.6(3)	Li2-O2-Zn2	88.7(2)
Li1-O4-C13	130.5(3)	Li2-O3-Zn1	91.6(2)
Li1-O1-Zn1	90.12(18)	Li2-O4-Zn2	90.8(2)
Li1-O1-Zn2	89.5(2)	Zn1-O1-C1	120.2(2)
Li1-O3-Zn1	92.50(19)	Zn1-O2-C5	121.9(2)
Li1-O4-Zn2	91.25(19)	Zn1-O3-C9	118.3(2)
Li1-O3-Li2	85.1(3)	Zn1-O1-Zn2	94.95(10)
Li1-O4-Li2	84.4(3)	Zn1-O2-Zn2	94.47(10)
Li2-O2-C5	131.2(3)	Zn2-O1-C1	120.2(2)
Li2-O3-C9	130.6(3)	Zn2-O2-C5	121.7(2)
Li2-O4-C13	127.2(3)	Zn2-O4-C13	120.7(3)

The structures observed for products **6**–**8**, formed by reaction of pyridylamines **1** and **2**, made it desirable to investigate the effects of employing the more sterically congested amine substrate $(2\text{-}C_5H_4N)N(H)(2,6\text{-}Xy)$ (**3**). This led to the isolation and characterisation of a significantly different product, the composition and structure of which may be of importance not only in understanding the chemical processes active in the reaction of **3**, but also in those of both **1** and **2**. X-ray diffraction reveals that the crystals deposited from solution after dry aeration of the product(s) of reaction between **3**, $ZnMe_2$ and *t*BuLi are composed of the pseudo-cubic lithium triorganozincate dimer $[\{THF \cdot [Li(tBu)OZn(OtBu)Me]\}_2]$ (**9**; Figure 4, Table 4). Whereas the solid-state structure of **7** revealed significantly asymmetric bis(*tert*-butoxy) capping of an Li_2Zn triangular fragment, that of **9** incorporates asymmetric *mono*-capping both of two Li_2Zn groups and of two $LiZn_2$ fragments (with concomitantly extended non-bonding *t*BuO⋯O*t*Bu distances; mean 2.845 Å). In the former case (μ_3-O3)-Li1-Li2-Zn1 and (μ_3-O4)-Li1-Li2-Zn2 moieties reveal mean Li–O and Zn–O distances of 1.973 Å and 2.017 Å, respectively, whereas in the latter case ((μ_3-O1)-Li1-Zn1-Zn2 and (μ_3-O2)-Li2-Zn1-Zn2) mean M–O distances are longer, at 2.010 Å (M = Li) and 2.063 Å (M = Zn), with the lithium–oxygen interactions dramatically extended relative to their (already long) analogues in **7**.[32] Notably, each of the four *tert*-butoxy fragments deviate from the normal to the plane described by the three metal centres to which they each bond. The reorientations now take two distinct forms depending on whether the alkoxy group is capping an Li_2Zn or an $LiZn_2$ triangle. In the former case, tilting of the group directly towards the zinc centre (mean C-O-(Li_2Zn plane) 80.7°) replicates the behaviour noted in **7**, while in the latter case the group tilts such as to bisect the Zn-O-Zn angle (mean C-O-($LiZn_2$ plane) 82.3°). Lastly, the unreacted ZnMe groups in **9** contrast with the ZnOMe fragments noted in both **6** and **8**. While further studies are required to elucidate the evidently complex reactions undergone by systems of this type, it seems reasonable to propose that the syntheses of species such as **6**-**9** are inter-related. The isolation and structural characterisation of both **6** and **7** from the same reaction mixture establishes that their chemistries are intimately linked. Furthermore, removal of solvent from the oxygenated reaction mixture **1**/$ZnMe_2$/*t*BuLi yields a microcrystalline mixture which NMR spectroscopy suggests contains both **6** and **9** (although **7** was not obviously observable); likewise, the equivalent treatment of a **2**/$ZnMe_2$/*t*BuLi reaction mixture affords both **8** and **9**.

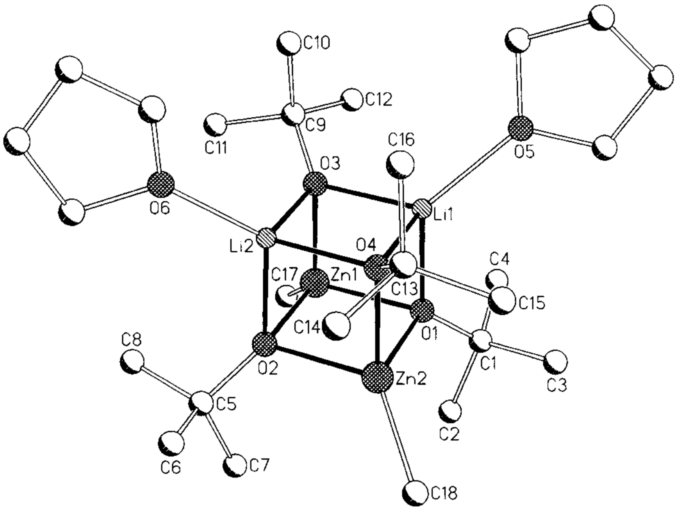


Figure 4. Molecular structure of pseudo-cubic dimer **9**; hydrogen atoms and minor THF disorder omitted.

Surprisingly, replacement of R = Ph (**1**), 3,5-Xy (**2**), or 2,6-Xy (**3**) with R = Bz (**4**, Bz = benzyl) in $(2\text{-}C_5H_4N)N(H)R$ affords neither the structural analogue of **6** nor that of **7**.[33] Instead a non-donor solution of **4** can be sequentially treated with $ZnMe_2$, *t*BuLi and dry air (P_2O_5) to afford a solution from which two crystalline compounds deposit. Both of these species could be satisfactorily characterised after their mechanical separation, with ^{1}H NMR spectroscopy verifying that one of the two products was unsolvated *t*BuOLi **10a**. X-ray crystallography reveals that the remaining species is not a mixed-metal compound but is, instead, the trigonal-pyramidal zinc complex $[(\mu_4\text{-O})Zn_4\{N(2\text{-Pyr})Bz\}_6]$ (**10b**; there is only one third of **10b** in the asymmetric unit along with one third of a lattice toluene molecule; Figure 5 and Table 5). The complex adheres to the beryllium acetate structure[34] with a non-bonded trigonal arrangement of three Zn centres forming the pyramid base (Zn1A···Zn1B 3.130(2) Å) each edge of which is spanned by a $[N(2\text{-}C_5H_4N)Bz]^-$ residue (Zn–N-$(2\text{-}C_5H_4N)$ 2.069(7), Zn–NBz 1.984(7) Å). The fourth zinc centre (Zn2) constitutes the C_{3v} cluster apex and is stabilised only by the pyridyl N-centres of the remaining organic ligands (Zn2–N$(2\text{-}C_5H_4N)$ 2.045(7) Å). Each of these three organic groups spans one non-bonded Zn1···Zn2 (3.089(2) Å) pyramid edge (Zn1–NBz 2.002(7) Å). Within the Zn_4 cluster, an approximately tetrahedral oxo-dianion is encapsulated (mean Zn–O 1.903 Å; mean Zn-O-Zn 108.9°). While $(\mu_4\text{-O})$-Zn_4 tetrahedra have been known for some time, **10b** is rendered highly unusual by virtue of its mode of synthesis. Unlike previous examples of oxo-encapsulation by Zn_4 tetrahedra it is afforded by exposure of a mixed Li–Zn system to oxygen. In contrast, the formation of, for example, $[(\mu_4\text{-O})Zn_4\{O_2CNEt_2\}_6]$,[35] $[(\mu_4\text{-O})Zn_4(7\text{-aza-indole})_6]$,[36] $[(\mu_4\text{-O})Zn_4(O_2CR)_6]$ (R = *t*Bu, Ph), $[(\mu_4\text{-O})Zn_4(1\text{-methylimidazoline-2-thione})_6]$, $[(\mu_4\text{-O})Zn_4\{N(Ph)C(H)NPh\}_6]$,[37] and the fused tetrahedra $[(\mu_4\text{-O})Zn_4R_4\{NMe(CH_2)_3NMe\}_4]$ (R = Me, Et),[38] derives from the deliberate introduction to the organometallic system either of carbon dioxide[35] or, more commonly, of water.[36–38]

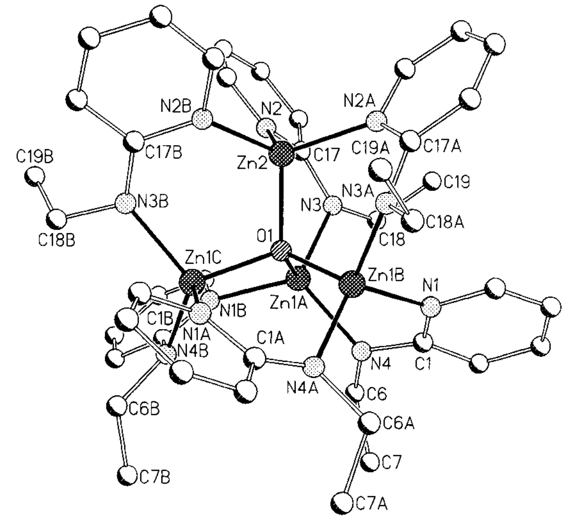


Figure 5. Molecular structure of the $(\mu_4\text{-O})Zn_4$-based tetrahedron **10b**; hydrogen atoms and lattice toluene molecule omitted and only the *ipso*-C positions of the phenyl rings are shown.

Table 5. Selected bond lengths [Å] and angles [°] for **10b**.

Zn1A–O1	1.905(3)	Zn1A–N4	1.984(7)
Zn2–O1	1.902(8)	N1–C1	1.369(10)
Zn1B–N1	2.069(7)	N4–C1	1.356(10)
Zn2–N2	2.045(7)	N2–C17	1.374(10)
Zn1A–N3	2.002(7)	N3–C17	1.357(10)
Zn1A-O1-Zn1B	110.5(2)	N2-Zn2-N2A	111.59(17)
Zn1A-O1-Zn2	108.4(2)	Zn1A-N3-C17	121.5(5)
O1-Zn1A-N3	109.4(3)	Zn2-N2-C17	124.1(5)
O1-Zn2-N2	107.26(18)	N2-C17-N3	116.9(7)

Employment of the less sterically demanding reagent $(2\text{-}C_5H_4N)N(H)Me$ (**5**) results in the observation of significant structural modification in the only isolable reaction product.[33] X-ray crystallography reveals the unique, distorted octahedral oxo-encapsulation complex to be $[t\text{Bu}(\mu_3\text{-O})Li_3(\mu_6\text{-O})Zn_3\{N(2\text{-}C_5H_4N)Me\}_6]$ (**11**; Figure 6, Table 6)—one third of which is related to the other two thirds by symmetry—for which formulation there is a single THF molecule in the lattice. Capping of the Li_3 face of the distorted octahedron by a $(\mu_3\text{-O})t$Bu group implicates the insertion of an oxygen atom into a Li–C(*t*Bu) bond (Li–O2 1.849(14) Å, Li-O2-Li 83.7(7)°).[31] The Li–O2 distance is considerably shorter than that for the $Li_2(\mu_3\text{-O})t$Bu unit in **7** and those for the $Li_2(\mu_3\text{-O})t$Bu and $Li(\mu_3\text{-O})t$Bu moieties in **9**. The three

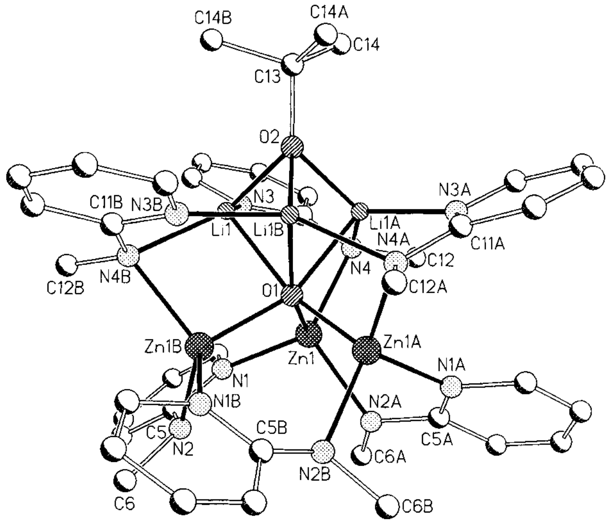


Figure 6. Molecular structure of the $(\mu_6\text{-O})Li_3Zn_3$-based distorted octahedron **11**; hydrogen atoms and lattice THF molecule omitted for clarity.

Table 6. Selected bond lengths [Å] and angles [°] for oxo-encapsulation complex **11**.

Zn1–O1	1.944(4)	Li1–O1	2.074(13)
Zn1–N1	2.039(6)	Li1–O2	1.849(14)
Zn1–N2A	2.050(7)	Li1–N3	2.071(14)
Zn1–N4	2.065(7)	Li1–N4	2.160(13)
Zn1···Li1	2.755(12)	Li1···Li1	2.47(2)
Zn1···Li1A	2.992(12)	Zn1···Zn1A	3.0070(19)
Li1-O1-Li1A	73.0(6)	O1-Li1-N4B	91.2(5)
Li1-O1-Zn1	96.2(4)	O1-Zn1B-N1B	113.6(2)
Li1-O1-Zn1A	158.8(5)	O1-Zn1B-N4B	97.9(3)
Li1-O1-Zn1B	86.5(3)	O1-Zn1B-N2	111.7(3)
Li1-O2-C13	129.6(4)	N1-Zn1-N2A	102.5(3)
Li1-O2-Li1A	83.7(7)	Zn1-O1-Zn1A	101.4(3)
Li1-N3-C11	123.3(7)	Zn1-N1-C5	123.6(5)
Li1-N4B-C11B	112.3(7)	Zn1-N2A-C5A	119.1(6)
Li1-N4B-Zn1B	81.4(4)	Zn1-N4-C11	108.7(6)
O1-Li1-O2	86.2(6)	N1-C5-N2	116.4(7)
O1-Li1-N3	108.0(6)	N3-C11-N4	115.4(7)

lithium centres bridge between this oxygen atom and the μ_6-encapsulated O^{2-} ion (Li–O1 2.074(13) Å, Li-O1-Li 73.0(6)°) and this in turn bonds to the three zinc centres (Zn–O1 1.944(4) Å, Zn-O1-Zn 101.4(3)°). The result of this bonding arrangement is the formation of a molecular $(\mu_6\text{-O})M_3M'_3$ distorted octahedron which is *fac*-isomeric. Whereas existing examples of molecular μ_6-O heterobimetallic octahedra are known, those which have been reported have all revealed either MM'_5 ($TiMo_5$)[39] or $M_2M'_4$ (e.g. Ba_2Y_4,[40] Bi_2Na_4,[41] Sb_2K_4,[42 Sb_2Na_4,[43] Zr_2Co_4[44] and Zr_2K_4[45]]) formulations. Furthermore, while the vast majority of lithium-containing μ_6-O octahedra have been homometallic,[46] just two reports exist of such heterobimetallic μ_6-O octahedral complexes. Thus, the 2:1 adduct $[RuH(SiHPh_2)(CO)X_2]_2[Li_2Ru_4OCl_8X_4]$ ($X = PtBu_2Me$) incorporates a *trans*-isomeric $(\mu_6\text{-O})Li_2Ru_4$ core,[47] while $[Li_3(\mu_6\text{-O})Ba_3(\mu_6\text{-O})\{(thf)_3Ba_3\}(OtBu)_{11}]$ incorporates two oxide centres—one inside a Ba_6 octahedron and the other in a Li_3Ba_3 prismane.[48]

The coordination spheres of both Li and Zn centres in **11** are completed by $[N(2\text{-Pyr})Me]^-$ ligands. Three of these residues span the 3.007(2) Å Zn···Zn non-bonding distances in the lower tier of the cluster (Zn–N1 2.038(7) Å, Zn–N2 2.050(7) Å). The remaining organic residues circumscribe the non-bonding Li_3 (Li···Li 2.47(2) Å) upper tier. They are orientated such that their N-pyridyl centres are precisely in the Li_3 plane, while their NMe groups span non-bonding heterobimetallic (Li···Zn 2.75(1) Å) distorted octahedron edges (Zn1–N4 2.065(7) Å). Hence, each upper tier organic residue participates in one Li-O-Zn-N four-membered ring and one M-O-M′-N-C-N six-membered ring, where the deprotonated N centre along with the Zn and (μ_6-O) centres are common to both heterocycles. An sp^2 orbital on the deprotonated N centre of each upper-tier anion almost bisects the Li-N(Me)-Zn bond angle (N3-C11-N4-M torsional angle 42.8° (M = Li1A) and 45.4° (M = Zn1)) with the consequent mismatch in orientation of the NMe-centred lone pair with the Li^+ ion in the upper tier probably being responsible for the differing $Li\text{–}N(2\text{-}C_5H_4N)$ and Li–NMe bond lengths (2.071(14) Å and 2.160(13) Å, respectively). This variability in amide coordination contrasts with the uniformly μ_2-[41, 44] or μ_3-bridging[40–43, 45, 47] modes adopted by ligand heteroatoms in previously reported μ_6-O molecular heterobimetallic octahedra.

The mode of oxo-insertion responsible for formation of the $Li_3(\mu_3\text{-O})tBu$ component of **11** inevitably leads to comparisons with the formation of $(\mu_3\text{-O})MM'_2$ fragments **6**, **8** and **9** (see above). However, the observation of oxo-encapsulation in **11** also points to a relationship with **10b**. The structures of both compounds reveal convoluted arrangements of six-membered M-O-M′-N-C-N heterocycles which result from the coordination of $[N(2\text{-}C_5H_4N)R]^-$ ligands. Whereas the structures of **6**, **7** and **8** all incorporate arrays of LiOZnNCN (i. e. M = Li, M′ = Zn) heterocycles, it is noteworthy that in the structure of **10b** both M and M′ are zinc, while both homometallic (M = M′ = Zn or Li) and heterometallic (M = Li, M′ = Zn) motifs are noted in that of **11**. However, **10b** and **11** share a further, unique similarity. The two species reveal almost identical $Zn_3[N(2\text{-}C_5H_4N)R]_3$ basal tiers (as represented in Figures 5 and 6), whilst the remaining three amide ligands exhibit significant variability between the two structures. The orientation which they adopt when coordinating to apical Zn2 in **10b** results in their pyridyl N centres bonding only to this zinc centre, rendering it approximately tetrahedral, with their deprotonated N centres bonding only to basal Zn1. However, in **11** the upper-tier ligands are orientated such that the pyridyl N centres lie almost exactly in the Li_3 plane, deviating from it by only 0.04 Å. In contrast to the structure of **10b** stabilisation of adjacent lithium centres by NR groups also takes place, with the result that these Lewis base N centres bridge to the basal Zn tier. In consequence both **10b** and **11** can be viewed as empirically incorporating a $\{(\mu_3\text{-O})Zn_3[N(2\text{-}C_5H_4N)R]_6\}^{2-}$ ligand. Flexibility in the orientations demonstrated by the upper tier of $[N(2\text{-}C_5H_4N)R]^-$ groups means that this chelating dianion is capable of exhibiting variable denticity-acting either as a tetradentate donor to the R_3-symmetry Zn^{2+} cation in **10b** or as a heptadentate donor to the C_{3v}-symmetry $[Li_3(\mu_3\text{-O})tBu]^{2+}$ cation in **11**.

Conclusion

Elucidation of the structural characteristics of the mixed Li–Zn precursors to compounds **6–12** and improving our understanding of the complex mechanisms by which they form represent major goals, and will be reported subsequently. However, the reproducibility with which **6–12** can be synthesised by the exposure of reaction mixtures to dry air (P_2O_5), in conjunction with recent work on the selective and controlled oxygenation of mixed Li–Al systems, strongly suggests that molecular oxygen[29] and not moisture[36–38] is the oxo-source. Indeed, we have recently established that the syntheses of **6–8** can be successfully reproduced by using O_2 as the oxygen source and we are presently seeking to further optimise reaction conditions. Results point clearly to two modes of selective oxygenation being dominant in systems of the type reported here. While the insertion of oxygen into a Zn–C(Me) bond is revealed by the presence of MeO fragments in both **6** and **8**, the observation of O*t*Bu groups in **7**, **10b** and **11**, as well as the incorporation in **9** of unreacted ZnMe groups (and also *t*BuO fragments) suggests competition between the oxophilicity of lithium and zinc. Finally, oxo-encapsulation is revealed both in the homometallic beryllium acetate structure of **10b** and also (in competition with insertion into M–C bonds) in **11**. The nature and extent of competition, both between methoxy and *tert*-butoxy formation and also between oxo-insertion and oxo-encapsulation is also being probed theoretically.[29b]

Experimental Section

Methods and materials: All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen or argon, using standard double manifold and glove-box techniques. Where appropriate the treatment of air-sensitive reaction mixtures with oxygen was achieved using air which had been pre-dried over P_2O_5 (Lancaster). All other chemical reagents were used as received from Aldrich without further purification. Toluene, THF and hexane were distilled off sodium or sodium/potassium amalgam immediately prior to use. NMR data were collected on a Bruker DRX 500

FT NMR spectrometer (operating at 500.05 MHz for ^{1}H). Chemical shifts are quoted relative to TMS at δ 0.00.

Synthesis and characterisation

THF · [Li(Me)OZn{N(2-C$_5$H$_4$N)Ph}$_2$] (6) and (THF · Li)$_2$[{(*t*Bu)O}$_2$Zn{N(2-C$_5$H$_4$N)Ph}$_2$] (7): $ZnMe_2$ (0.5 mL, 1 mmol, 2 M in toluene) was added to a solution of 2-anilinopyridine (**1**, 0.17 g, 1 mmol) in toluene (2 mL). After reaction had ceased the orange solution was chilled to −78 °C and *t*BuLi (0.59 mL, 1 mmol, 1.7 M in pentane) was added. The resultant solution was returned to room temperature and treated sequentially with toluene (1 mL), THF (1 mL) and dry air (P_2O_5) (until observable reaction ceased, ca. 1 min.). Filtration was followed by storage at room temperature for one week whereupon colourless needles of **6** and blocks of **7** were deposited. Mechanical separation allowed the characterisation of both compounds. **6**: Yield 61 % (by **1** consumed), m. p. > 300 °C; elemental analysis (%) calcd for $C_{31}H_{37}LiN_4O_3Zn$: C 63.59, H 6.32, N 9.57; found: C 62.94, H 6.23, N 9.63; ^{1}H NMR spectroscopy (500 MHz, CD_3CN): δ = 8.15 – 6.73 (m, 6H; Ar), 3.65 (m, 2H; THF), 3.23 (s, 1H; OMe), 1.80 (m, 2H; THF), 1.17 (s, 4H; *t*Bu from trace **7**). **7**: Yield 10 % (by **1** consumed), m. p. 168 – 170 °C; elemental analysis (%) calcd $C_{38}H_{52}Li_2N_4O_4Zn$: C 64.50, H 7.36, N 7.92 %; found: C 64.31, H 7.27, N 8.07; ^{1}H NMR spectroscopy (500 MHz, CD_3CN): δ = 8.14 – 5.57 (m, 9H; Ar), 3.64 (m, 4H; THF), 1.81 (m, 4H; THF), 1.14 (s, 18H; *t*Bu).

THF · [Li(Me)OZn{N(2-C$_5$H$_4$N)(3,5-Xy)}$_2$] (8): $ZnMe_2$ (0.5 mL) was added to a room-temperature solution of 2-(3,5-dimethylanilino)pyridine (**2**, 0.20 g, 1 mmol) in toluene (2 mL). Once reaction had ceased the solution was cooled to −78 °C whereupon *t*BuLi (0.59 mL) was added. Warming of the reaction mixture to room temperature afforded a suspension to which THF (1 mL) and dry air (P_2O_5) were added (ca. 1 min). Complete solvation was achieved by the addition of further THF (0.5 mL) after which storage at room temperature for 24 h afforded blocks of **8**. Yield 84 % (by **2** consumed), m.p. > 300 °C; elemental analysis (%) calcd for $C_{76}H_{92.5}Li_2N_8O_4Zn_2$: C 65.38, H 6.50, N 9.84; found: C 63.59, H 5.99, N 9.52; ^{1}H NMR spectroscopy (500 MHz, CD_3CN): δ = 8.14 – 7.14 (m, 6H; Ar), 6.80 – 6.64 (m, 1.5H; PhMe), 3.65 (m, 2H; THF), 3.50 – 3.28 (m, 1.2H; OMe), 2.33 (s, 6H; 3,5-Me), 2.27 (s, 1H; PhMe), 1.81 (m, 2H; THF).

[{THF · [Li(*t*Bu)OZn(O*t*Bu)Me]}$_2$] (9): $ZnMe_2$ (0.5 mL) was added to a solution of 2-(2,6-dimethylanilino)pyridine (**3**, 0.20 g, 1 mmol) in toluene (2 mL). The resultant orange solution was cooled to −78 °C and treated with *t*BuLi (0.59 mL) before being returned to room temperature. The addition of THF (1 mL) was followed by treatment with dry air (P_2O_5) (ca. 1 min) and the addition of hexane (1 mL). Reduction of the solvent volume by one half, followed by storage at −30 °C for two weeks, resulted in the growth of crystalline **9**. Yield 85 % (by *t*BuLi consumed), m. p. 153 – 155 °C; elemental analysis (%) calcd for $C_{13}H_{29}LiO_3Zn$: C 51.15, H 9.51; found: C 51.04, H 8.97; ^{1}H NMR spectroscopy (500 MHz, CD_3CN): δ = 3.65 (m, 4H; THF), 1.81 (m, 4H; THF), 1.20 (s, 9H; *t*Bu), 1.17 (s, 9H; *t*Bu), −0.79 (s, 3H; ZnMe).

***t*BuOLi (10a) and [(μ_4-O)Zn$_4${N(2-C$_5$H$_4$N)Bz}$_6$] (10b)**: $ZnMe_2$ (0.5 mL) was added to a stirred solution of 2-(benzylamino)pyridine (**4**, 0.18 g, 1 mmol) in toluene (5 mL) at −78 °C. After 30 min the mixture was warmed to −40 °C and *t*BuLi (0.59 mL) was added. After being allowed to warm to room temperature the mixture was treated with dry air (P_2O_5) (ca. 1 min) and then refluxed and stored at ambient temperature for 24 h whereupon needles of **10a** (by ^{1}H NMR spectroscopy) and blocks of **10b** formed. Mechanical separation allowed the characterisation of **10b**. Yield 42 % (by **4** consumed), m. p. 140 °C (decomp); elemental analysis (%) calcd for $C_{79}H_{74}N_{12}OZn_4$: C 64.53, H 5.04, N 11.44; found: C 64.96, H 5.16, N 11.34; ^{1}H NMR spectroscopy (500 MHz, CD_3CN): δ = 7.40 – 6.46 (m, 20H; Ar + *Ph*Me), 4.56 (s, 4H; CH_2), 2.33 (s, 1H; Ph*Me*).

[*t*Bu(μ_3-O)Li$_3$(μ_6-O)Zn$_3${N(2-C$_5$H$_4$N)Me}$_6$] (11): $ZnMe_2$ (0.5 mL) was added to a stirred −78 °C solution of 2-(methylamino)pyridine (**5**, 0.11 g, 1 mmol) in hexane (1 mL). After 30 min *t*BuLi (0.59 mL) was added. Treatment of the room-temperature mixture with dry air (P_2O_5) (ca. 1 min) and the addition of THF (0.08 mL) was followed by storage at room temperature for one week whereupon blocks of **11** formed. Yield 32 % (by **5** consumed), m. p. > 300 °C; elemental analysis (%) calcd for $C_{44}H_{59}Li_3N_{12}O_3Zn_3$: C 51.69, H 6.45, N 13.45; found: C 50.68, H 6.48, N 12.64; ^{1}H NMR spectroscopy (500 MHz, [^{2}H$_8$]THF): δ = 8.00 – 6.01 (m, 24H; Ar), 3.65 (m, 4H; THF), 2.81 (s, 9H; NMe), 2.53 (br, m, 9H; NMe), 1.80 (m, 4H; THF), 1.12 (s, 9H; *t*Bu).

X-ray crystallography

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-157415 (**6**), CCDC-157416 (**7**), CCDC-157417 (**8**), CCDC-157418 (**9**) and CCDC-182/1748 (**10b** and **11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Data for **6** · 0.5 THF, **7**, **8** · 0.5 PhMe, **9**, **10b** · PhMe and **11** · THF were collected on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device. The positions of the metal atoms and their first coordination spheres were determined by direct methods and refined against F^2 using SHELXL-97.[49] All non-hydrogen atoms were found by successive iterations of least-squares refinement and treated anisotropically unless otherwise stated. Hydrogen atoms were added in calculated positions and allowed to ride on their parent atoms.

Table 7. Crystallographic data for **6 – 9, 10b** and **11**.

	6 · 0.5 THF	**7**	**8** · 0.5 PhMe	**9**	**10b** · PhMe	**11** · THF
formula	$C_{31}H_{37}LiN_4O_3Zn$	$C_{38}H_{52}Li_2N_4O_4Zn$	$C_{76}H_{92.5}Li_2N_8O_4Zn_2$	$C_{26}H_{58}Li_2O_6Zn_2$	$C_{79}H_{74}N_{12}OZn_4$	$C_{11}H_{14.75}Li_{0.75}N_3O_{0.75}Zn_{0.75}$
M_r	585.96	708.09	1326.70	611.34	1468.98	255.24
crystal system	monolinic	monolinic	monolinic	monolinic	cubic	cubic
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Ia3$	$P2_13$
a [Å]	14.4640(3)	15.4531(5)	11.6732(3)	9.5863(3)	30.8060(7)	16.694(10)
b [Å]	23.9920(14)	15.1578(7)	20.5696(5)	18.3249(4)	30.8060(7)	16.694(10)
c [Å]	8.6790(8)	17.8974(6)	15.4684(4)	19.6629(7)	30.8060(7)	16.694(10)
β [°]	91.58(2)	114.834(2)	110.018(2)	101.100(2)	90	90
V [Å^3]	2901.8(3)	3804.5(2)	3489.77(15)	3389.52(18)	29235.2(12)	4882.0(10)
Z	4	4	2	4	16	4
ρ_{calcd}	1.341	1.236	1.263	1.198	1.335	1.389
radiation [Å]	$Mo_{K\alpha}$, 0.71069	$Mo_{K\alpha}$, 0.71069	$Mo_{K\alpha}$, 0.71069	$Mo_{K\alpha}$, 0.71069	$Mo_{K\alpha}$, 0.71069	$Mo_{K\alpha}$, 0.71069
μ [mm^{-1}]	0.885	0.688	0.742	1.446	1.350	1.513
T [K]	180(2)	180(2)	180(2)	180(2)	180(2)	180(2)
measured refl.	8520	24653	20623	24752	8240	20356
unique refl.	5040	10989	7909	5923	4297	2128
θ [°]	< 24.96	< 30.00	< 27.46	< 24.99	< 25.02	< 22.44
R_{int}	0.0316	0.0470	0.0509	0.0695	0.0886	0.0744
$R(F)$, $wR(F^2)$	0.0540, 0.1410	0.0628, 0.1879	0.0466, 0.1725	0.0413, 0.1657	0.0849, 0.1987	0.0744, 0.2093
parameters	337	518	459	395	276	205
GoF	1.022	1.081	1.153	1.220	0.993	1.190
residual electron density [eÅ^{-3}]	± 0.82	± 0.78	± 1.31	± 1.73	± 1.45	± 1.02

For **6**·THF, all of the atoms of a disordered molecule of lattice THF were not treated anisotropically; this disorder was not modelled. The carbon atoms of the two disordered THF ligands and the disordered methyl carbon atoms in one of the *tert*-butoxy groups of **7** were not treated anisotropically. The THF carbon atoms were modelled over two sites and refined at either 0.43:0.57 or 0.61:0.39 occupancy; disorder in the methyl group carbon centres was modelled over two sites and refined at 0.72:0.28 occupancy in **8**·PhMe. Each of the carbon atoms in the THF ligands were disordered and this was modelled over two conformations with the carbon atoms being refined at 0.69:0.31 occupancy. For **9**, all of the carbon atoms of the two THF ligands were disordered; each disorder was modelled over two conformations and the carbon atoms refined at either 0.62:0.36 or 0.66:0.34 occupancy. Disordered lattice toluene was not treated anisotropically in **10b**·PhMe—diffraction data being of insufficient quality to allow satisfactory modelling of this disorder—a constraint being applied to generate a rigid hexagonal ring. For **11**·THF, the atoms of the lattice THF molecule were not refined anisotropically and the bond lengths in this molecule were restrained (to be within 0.01 Å of one another) (see Table 7).

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