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New motifs in lithium zincate chemistry: a solid-state structural study of PhC(O)N(R)ZnR′$_2$Li·2thf (R, R′ = alkyl, aryl) and [PhC(O)N(Ph)Li·thf]·[PhC(O)N(Ph)Zn(Bu^t)$_2$Li·thf]

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The facile reaction of ZnMe$_2$ with secondary carboxylic amides of the type PhC(O)N(R)H (R = Me **14**, Pr^i **15**, Ph **16**) yields PhC(O)N(R)ZnMe (R = Me **17**, Pr^i **18**, Ph **19**). These complexes describe a hexamer (for **17**) and tetramers (for **18** and **19**) in the solid state which are best viewed as stacks of cyclic trimers and dimers, respectively. In turn, **17**–**19** react with Bu^{t}Li to afford either the lithium zincate PhC(O)N(R)Zn(Bu^t)$_2$Li·2thf (R = Me **20**, Pr^i **21**) or the co-complex [PhC(O)N(Ph)Li·thf]·[PhC(O)N(Ph)Zn(Bu^t)$_2$Li·thf] **22**. In the solid state both **20** and **21** reveal dimeric structures based on a (LiO)$_2$ core in which each alkali metal centre is doubly thf-solvated and trivalent zinc centres reside peripheral to the cluster. The structure of **22** reveals an adduct in which a dimeric lithium (carboxylic) amide core interacts with two PhC(O)N(Ph)Zn(Bu^t)$_2$Li molecules, affording a structure intermediate between a ladder and an "open" pseudo-cubane. This is the first full characterisation of a complex between an alkali metal zincate and another organometallic species and it affords new insights into how these two classes of molecule interact. The straightforward formation of [PhC(O)N(R)ZnMe$_2$]$^-$ (R = Me **23**, Ph **24**) ions has been successfully achieved by treating the appropriate lithium carboxylic amide with ZnMe$_2$. In the solid-state, PhC(O)N(Ph)ZnMe$_2$Li·2thf **24** is revealed to be isostructural with **20** and **21**.

Although lithium-containing heterobimetallic species are widely used in synthetic chemistry,[1,2] a recent survey of the literature[2] has shown that the structural chemistry of lithium organozincates is not well documented. While reports exist of ion-separated triorganozincates (ZnR$_3$$^-Li^+$) which have been isolated from various Lewis base media,[3,4] ion-association has been reported in (Me$_3$Si)$_2$N(Me$_3$SiCH$_2$)$_2$ZnLi·tmeda (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[4] More common than the Zn(μ-N)Li motif noted for this complex are Zn(μ-C)$_n$Li (n = 1, 2) fragments.[5,6] Most recently, (MeCN)Cl(μ$_3$,η^2-ddbfo)$_2$(μ,η^2-ddbfo)$_3$ZnLi$_4$ (ddbfo = 2,3-dihydro-2,2-dimethyl-7-benzofuranoxide) has been found to be based on an array of Zn(μ-O)$_2$Li-based rings.[7]

The oxygenation of organometallic compounds has been probed by the synthesis of mixed s-block metal species[8] and by the derivatisation of certain lithium aluminates.[9] Sequential reaction of di(*p*-tolyl)formamidine with Bu^{n}Li and ZnCl$_2$ in the presence of trace oxygen has given the N-oxygenated formamidinate [(*p*-Tol)N(O)C(H)N(*p*-Tol)]$_6$Zn$_3$(μ$_5$-O)Li$_2$[10] and ZnMe$_2$ has been reacted with 2-pyridylamines [HN(2-C$_5$H$_4$N)-R, R = Ph **1**, 3,5-xy **2** (xy = xylyl), 2,6-xy **3**, Me **4**], Bu^{t}Li and dry air to give a disparate set of heterometallic complexes. These include [Ph(2-C$_5$H$_4$N)N]$_2$Zn[μ$_3$-O(Bu^t)]$_2$(Li·thf)$_2$ **5**, which forms concomitantly with {[Ph(2-C$_5$H$_4$N)N]$_2$ZnO(Me)Li·thf}$_2$ **6**—the 3,5-xy analogue (**7**) of which has also been reported.[11] The structures of **6** and **7** imply the formal reaction of [R(2-C$_5$H$_4$N)N]$_2$ZnMe$^-$ and strength has been lent to this view by the recent characterisation and oxygenation of the related anion [Ph(2-C$_5$H$_4$N)N]$_2$ZnR$^-$ (R = Bu^n, Bu^t).[12] Varying the steric demands of the amine substrate has yielded pseudo-cubic [(Bu^{t}O)$_2$ZnMe]$_2$(Li·thf)$_2$ **8**, and also the oxide-alkoxide [Me(2-C$_5$H$_4$N)N]$_6$Zn$_3$(μ$_6$-O)Li$_3$(μ$_3$-O)Bu^t **9**.[11] Related work with *N*,*N*′-diphenylbenzamidine[13] (HAm) **10** has led to the isolation of [Am$_2$ZnO(Me)Li·thf]$_2$ **11** from thf with toluene affording both pseudo-octahedral (μ$_6$-O)(Am$_3$ZnLi$_2$)$_2$ **12** and [(Bu^{t}OZnMe)$_3$-(Bu^{t}OLi)]$_\infty$ **13**.[14]

We report here the conversion of PhC(O)N(R)H (R = Me **14**, Pr^i **15**, Ph **16**) into the methylzinc carboxylic amides PhC(O)-N(R)ZnMe (R = Me **17**, Pr^i **18**, Ph **19**). These have been reacted with Bu^{t}Li to afford either lithium zincates PhC(O)N(R)Zn-(Bu^t)$_2$Li·2thf (R = Me **20**, Pr^i **21**) or the zincate/(carboxylic) amide co-complex [PhC(O)N(Ph)Li·thf]·[PhC(O)N(Ph)Zn-(Bu^t)$_2$Li·thf] **22**. Zn(Bu^t)$_2$ evolution is implied by the formation of the PhC(O)N(Ph)Li component of this last species and it is in this context that the synthesis and characterisation PhC(O)-N(R)ZnMe$_2$Li·2thf (R = Me **23**, Ph **24**) is discussed. Results presented here suggest for the first time that (LiO)$_n$ rings[9,15,16] can determine the structures of lithium zincates.

Results and discussion

The reaction of *N*-methyl benzamide **14** with ZnMe$_2$ in toluene results in CH$_4$ evolution. Reduction to dryness gives an amorphous material which ^{1}H NMR spectroscopy suggests to be PhC(O)N(Me)ZnMe **17** (Scheme 1) and storage of the reaction mixture at ambient temperature affords a crystalline material which analyses as the same species. Retention of the zinc-bonded methyl group is implied by the observation of singlets at δ −0.37 and −17.4 by ^{1}H and ^{13}C NMR spectroscopy, respectively. X-ray diffraction studies bear out the suggested stoichiometry, revealing a [PhC(O)N(Me)ZnMe]$_6$ aggregate for which there exist two molecules of lattice toluene. The oligomer is composed of *Z*-configured molecules and incorporates two, highly puckered, 12-membered (ZnNCO)$_3$ rings (top and bottom in Fig. 1; mean Zn–O = 2.061 Å, Table 1)

$$\mathrm{PhC(O)N(R)H + ZnMe_2 \xrightarrow{PhMe} {}^1/_n[PhC(O)N(R)ZnMe]_n}$$

R = Me **14**;
R = Pr^i **15**;
R = Ph **16**

R = Me, n = 6 **17**;
R = Pr^i, n = 4 **18**;
R = Ph, n = 4 **19**

Scheme 1

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Table 1 Selected bond lengths (Å) and angles (°) for (**17**)$_6$·2PhMe

Zn1–O1	2.082(3)	Zn3–N1	2.011(4)
Zn1–O3	2.062(3)	C1–O1	1.306(6)
Zn1–N2	2.010(4)	C1–N1	1.295(6)
Zn2–O1	2.063(3)	C10–O2	1.307(6)
Zn2–O2	2.086(3)	C10–N2	1.294(6)
Zn2–N3A	2.022(4)	C19–O3	1.302(6)
Zn3–O2A	2.057(3)	C19–N3	1.290(7)
Zn3–O3	2.089(3)		
O1–Zn1–O3	90.78(13)	Zn1–N2–C10	126.5(3)
Zn1–O3–Zn3	105.59(16)	N2–C10–O2	120.1(4)
O3–Zn3–N1	106.19(15)	Zn2–O2–C10	116.4(3)
Zn3–N1–C1	124.9(3)	O2A–Zn3–O3	91.48(13)
N1–C1–O1	119.4(4)	Zn2A–O2A–Zn3	105.16(14)
Zn1–O1–C1	116.7(3)	O2A–Zn2A–N3	106.70(15)
O1–Zn2–O2	91.15(13)	Zn2A–N3–C19	125.2(3)
Zn1–O1–Zn2	105.28(15)	N3–C19–O3	120.7(4)
O1–Zn1–N2	104.98(15)	Zn3–O3–C19	118.6(3)

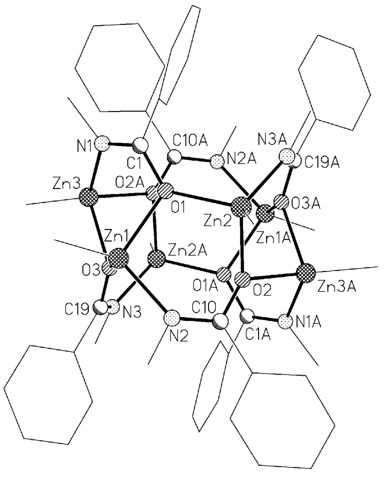


Fig. 1 Structure of (**17**)$_6$·2PhMe; lattice solvent and hydrogen atoms excluded.

with one ring being inverted and staggered relative to the other. Six longer interactions between the metal centres in one such trimer and the carbonyl O-centres in the other (mean Zn–O = 2.086 Å) link these two heterocycles and, in doing so, yield as many more 6-membered ZnNCOZnO rings.

The use of more sterically demanding *N*-isopropyl benzamide[17] **15** or benzanilide **16** in conjunction with $ZnMe_2$ has allowed the isolation and structural characterisation of the respective isostructural tetramers $[PhC(O)N(Pr^i)ZnMe]_4$ **18** and $[PhC(O)N(Ph)ZnMe]_4$ **19** (for which formulation there are two lattice toluene molecules) (Scheme 1, Figs. 2 and 3, Tables 2 and 3). Both **18** and **19** comprise two boat-configured $(ZnNCO)_2$ rings (top and bottom in Figs. 2 and 3). This motif is analogous to that seen in the $(LiOCO)_2$ core of a tetrameric 2,3-dimethylindole-based alkali metal carbamate complex.[18] Akin to **17**, these two metallocycles fuse to give a series of 6-membered rings through the formation of long Zn–O bonds.

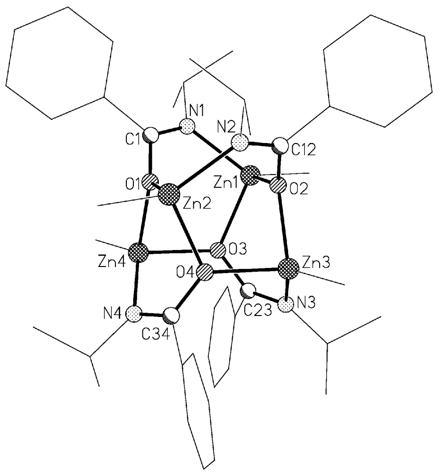


Fig. 2 The tetramer (**18**)$_4$; hydrogen atoms excluded.

Table 2 Selected bond lengths (Å) and angles (°) for (**18**)$_4$

Zn1–O2	2.072(3)	Zn4–O3	2.064(2)
Zn1–O3	2.071(3)	Zn4–N4	2.034(3)
Zn1–N1	2.028(3)	C1–O1	1.307(5)
Zn2–O1	2.063(3)	C1–N1	1.286(5)
Zn2–O4	2.086(2)	C12–O2	1.309(4)
Zn2–N2	2.028(3)	C12–N2	1.296(5)
Zn3–O2	2.073(2)	C23–O3	1.308(4)
Zn3–O4	2.067(3)	C23–N3	1.286(5)
Zn3–N3	2.031(3)	C34–O4	1.304(4)
Zn4–O1	2.084(3)	C34–N4	1.294(5)
O1–Zn4–O3	87.62(10)	O2–Zn1–O3	89.50(10)
Zn1–O3–Zn4	113.97(11)	Zn1–O2–Zn3	112.48(12)
O3–Zn1–N1	104.12(12)	O2–Zn3–N3	104.34(11)
Zn1–N1–C1	117.6(3)	Zn3–N3–C23	117.9(2)
N1–C1–O1	120.0(3)	N3–C23–O3	119.8(3)
Zn2–O1–C1	125.4(2)	Zn1–O3–C23	119.4(2)
O2–Zn3–O4	89.05(10)	O1–Zn2–O4	87.58(10)
Zn2–O4–Zn3	115.61(12)	Zn2–O1–Zn4	113.85(11)
O4–Zn2–N2	102.64(12)	O1–Zn4–N4	103.16(11)
Zn2–N2–C12	121.0(3)	Zn4–N4–C34	118.7(3)
N2–C12–O2	120.5(4)	N4–C34–O4	119.4(3)
Zn3–O2–C12	119.5(2)	Zn2–O4–C34	117.8(2)

Table 3 Selected bond lengths (Å) and angles (°) for (**19**)$_4$·2PhMe

Zn1–O1	2.068(2)	Zn4–O4	2.094(2)
Zn1–O2	2.090(2)	Zn4–N3	2.035(3)
Zn1–N2	2.037(3)	C29–O3	1.300(4)
Zn2–O3	2.081(2)	C29–N2	1.307(4)
Zn2–O4	2.064(2)	C1–O1	1.297(4)
Zn2–N4	2.050(3)	C1–N4	1.308(4)
Zn3–O2	2.068(2)	C43–O4	1.306(4)
Zn3–O3	2.088(2)	C43–N1	1.303(5)
Zn3–N1	2.044(3)	C15–O2	1.297(4)
Zn4–O1	2.077(2)	C15–N3	1.301(5)
O1–Zn1–O2	88.10(9)	O2–Zn3–O3	89.92(9)
Zn1–O1–Zn4	115.34(10)	Zn1–O2–Zn3	111.11(10)
O1–Zn4–N3	100.78(11)	O2–Zn1–N2	106.51(10)
Zn4–N3–C15	120.3(2)	Zn1–N2–C29	119.6(2)
N3–C15–O2	119.2(3)	N2–C29–O3	119.2(3)
Zn1–O2–C15	119.2(2)	Zn3–O3–C29	123.2(2)
O3–Zn2–O4	89.24(9)	O1–Zn4–O4	90.08(9)
Zn2–O3–Zn3	113.57(10)	Zn2–O4–Zn4	112.08(10)
O3–Zn3–N1	104.97(10)	O4–Zn2–N4	101.82(10)
Zn3–N1–C43	119.8(2)	Zn2–N4–C1	120.6(2)
N1–C43–O4	119.8(3)	N4–C1–O1	118.8(3)
Zn2–O4–C43	125.6(2)	Zn4–O1–C1	118.2(2)

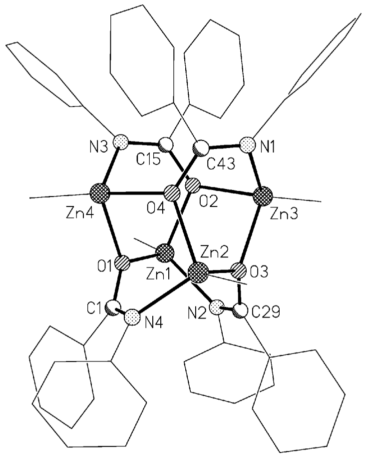


Fig. 3 The structure of (**19**)$_4$·2PhMe; lattice toluene molecules and hydrogen atoms excluded.

Given that the structure-types noted for complexes **17**–**19** would appear to be general for secondary alkylzinc carboxylic amides, it is surprising that they have not hitherto been noted in organozinc chemistry. This reflects the fact that, while neutral carboxylic amides have been used as external stabilising agents for $\mathrm{ZnX_2}$ salts,[19] few formally N-zincated carboxylic amides have been structurally characterised. While structures akin to those reported here have been previously postulated,[20] to the best of our knowledge only four N-zincated carboxylic amides have been studied in the solid state. These have all been ion-separated monomers, with the metal centre being N-stabilised *but not* O-stabilised by virtue of the employment of extensively coordinating, polyfunctional donors.[21] More generally, and in contrast to the structures of **17**–**19**, previously reported carboxylic amide–zinc complexes have revealed metal centre stabilisation to be either N- or O-based, with the two modes being mutually exclusive.[19,21]

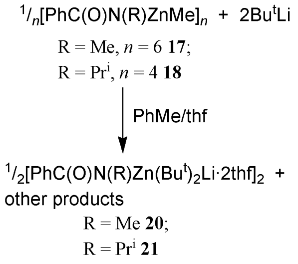
The treatment of **17** or **18** with $\mathrm{Bu^tLi}$ (1 equiv.) affords a single type of isolable product (Scheme 2). In both cases ^{1}H NMR spectroscopy points to R (= Me, $\mathrm{Pr^i}$) and $\mathrm{Bu^t}$ groups in a 1 : 2 ratio. For the *N*-methyl system, ^{1}H NMR spectroscopy reveals a singlet attributable to the NMe group. However, repeated analysis by ^{13}C and HMQC NMR spectroscopy fails to locate the corresponding carbon resonance (noted at δ 38.0 in **17**). In spite of this, the composition implied by NMR is borne out crystallographically. For R = Me, a complex of formulation $\mathrm{PhC(O)N(Me)Zn(Bu^t)_2Li{\cdot}2thf}$ **20** is revealed which is a dimer in the solid state (Fig. 4) and for which aggregate there exists one lattice toluene molecule. At the core of this dimer is a $\mathrm{(LiO)_2}$ ring which utilises the carboxylic amide O-centres and contains two bond types (mean Li1–O1, Li2–O2 1.935 Å; mean Li1–O2, Li2–O1 1.908 Å; Table 4). Whereas the previously reported lithium aluminate analogue of **20**—$\mathrm{PhC(O)N(Ph)AlMe_2(Bu^t)Li}$—revealed agostic stabilisation of the alkali metal centres,[9] comparable donation by Zn-bonded alkyl groups is precluded by thf solvation (two solvent molecules per $\mathrm{Li^+}$ ion). Lying exocyclic to the $\mathrm{(LiO)_2}$ core, the two organic ligands reside at 105.3° to each other with the crystallographic unit cell containing one of each of the two resulting stereoisomers. The Group 12 metal centres reveal distorted trigonal planar coordination with delocalisation affording a ligand whose ZnNCO backbone is precisely planar and which, in contrast to recently noted lithium aluminates bearing carboxylic amide ligands,[9] adopts *E*-configuration (*cf.* also *Z*-configured **17**)—implying that previous observations of *cis*-geometric 'ate complexes had their origins in electrostatic stabilisation of the alkali metal centres.[22] At 1.285 and 1.297 Å (mean), the relative lengths of C7 ··· O1, C23 ··· O2, C7 ··· N1 and C23 ··· N2 interactions point to some level of azaenolate character in **20**.[23] Indeed, in spite of the different modes of $\mathrm{Li^+}$ stabilisation revealed, these azaenolate characteristics compare closely with those seen in the dimer of $\mathrm{PhC(O)N(Ph)AlMe_2(Bu^t)Li}$.[9] An average Zn–N distance of 2.089 Å and a mean C–Zn–C angle of 136.89° are observed. One example of a bis(quaternary carbon)-bonded zinc centre has previously been fully characterised [in the carbenoid product of reaction between 1,3,4,5-tetramethylimidazol-2-ylidene and bis(pentamethylcyclopentadienyl)zinc][24] and, to the best of our knowledge, no $\mathrm{Zn(Bu^t)_2}$-containing systems have previously been studied crystallographically.

Table 4 Selected bond lengths (Å) and angles (°) for $\mathbf{(20)_2}{\cdot}\mathrm{PhMe}$

Li1–O1	1.936(6)	Li2–O6	1.961(6)
Li1–O2	1.910(6)	Zn1–N1	2.078(3)
Li1–O3	1.960(6)	Zn2–N2	2.100(3)
Li1–O4	1.963(6)	C7–O1	1.286(4)
Li2–O1	1.906(6)	C7–N1	1.299(4)
Li2–O2	1.934(6)	C23–O2	1.283(4)
Li2–O5	1.85(4)	C23–N2	1.295(4)
O1–Li1–O2	90.5(2)	Li1–O2–Li2	89.3(2)
O1–Li2–O2	90.7(2)	C9–Zn1–C13	135.88(19)
Li1–O1–Li2	89.3(2)	C25–Zn2–C29	137.89(18)

Table 5 Selected bond lengths (Å) and angles (°) for **21**

Li1–O1	1.974(4)	C1–O2	1.292(4)
Li1–O2	1.935(4)	C1–N1	1.316(6)
Zn1–N1	2.184(4)		
O2–Li1–O2A	91.3(3)	C11–Zn1–C11A	132.29(16)
Li1–O2–Li1A	88.7(3)		



Scheme 2

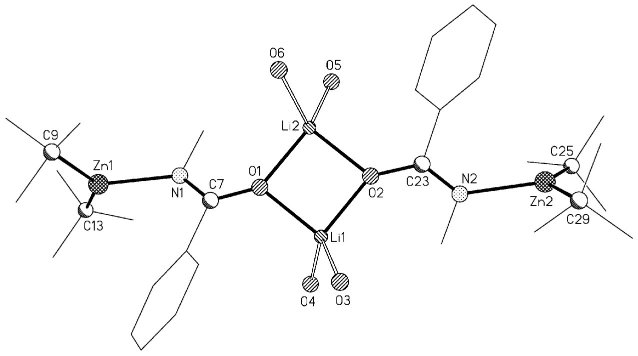


Fig. 4 Structure of $\mathbf{(20)_2}{\cdot}\mathrm{PhMe}$; hydrogen atoms, lattice toluene molecule and minor disorder omitted and only the thf O-centres shown.

The *N*-isopropyl system affords a dimeric product [$\mathbf{(21)_2}$] with crystallography showing organic ligands in each dimer that occupy two planes, the torsional angle between which is 94.4°. These ligands are each disordered over two orientations related by a mirror plane, such that in contrast to the structure of **20**, the asymmetric unit of **21** is racemically disordered. Nevertheless, the main structural features of this dimer are unambiguous. Like **20**, it incorporates a core $\mathrm{(LiO)_2}$ ring (Fig. 5, Table 5) relative to which the zinc centres lie exocyclic. The organic groups are again *E*-configured and reveal similar azaenolate characteristics to those seen in **20**. However, the observed Zn–N length [2.184(4) Å] is greater than that which results from the presence of sterically less demanding NMe groups in **20**, while at 132.29(16)° the C–Zn–C angle is smaller than that reported in the previous compound.

The treatment of PhC(O)N(Ph)H **16** with 1 equiv. $\mathrm{ZnMe_2}$ to give PhC(O)N(Ph)ZnMe **19** has already been described. However, instead of giving a precise analogue of either **20** or **21** the

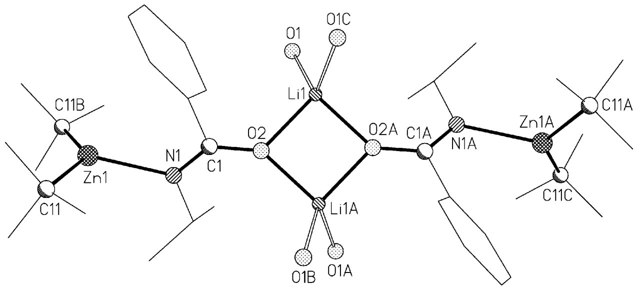
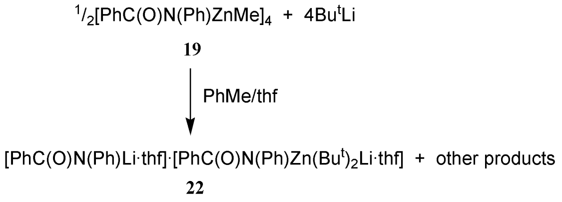


Fig. 5 Structure of $\mathbf{(21)_2}$; hydrogen atoms and disorder omitted and only the thf O-centres shown.

introduction of $\mathrm{Bu^tLi}$ incurs the formation of an unusual mixed-anion species. X-Ray crystallography reveals this to be a dimer based on the formulation $\mathrm{[PhC(O)N(Ph)Li{\cdot}thf]{\cdot}[PhC(O)N(Ph)Zn(Bu^t)_2Li{\cdot}thf]}$ **22** (Scheme 3, Fig. 6(a), Table 6), with the asymmetric unit containing two such aggregates—of which one representative dimer will be discussed in detail—along with uncoordinated thf (one molecule at half occupancy) and toluene (two molecules at full occupancy, five molecules at half occupancy, and half a molecule at full occupancy lying on an inversion centre) in the crystal lattice. These uncoordinated solvent molecules present two major analytical difficulties. Firstly, ^{1}H NMR spectroscopy indicates that they are readily lost *in vacuo* during isolation, with the spectrum suggesting the retention of only one molecule of lattice toluene per unit cell (elemental analysis is consistent with this partially desolvated formulation). Secondly, thermal motion exhibited by lattice solvent molecules incurs a high crystallographic *R*1 value of 0.0949. In spite of this, it is clear that the complete structure of co-complex **22** has been unambiguously determined. Akin to **20** and **21**, it is based on $\mathrm{(LiO)_2}$ rings. However, rather than incorporating an isolated metallocycle, **22** is based on three edge-fused $\mathrm{(LiO)_2}$ rings. Peripheral to this core are four molecules of coordinated thf and two types of anionic ligand. The formally N-lithiated carboxylic amide anions use their Group 15 charge centres to close four-membered OCNLi chelate rings with Li1/4 (mean Li–N 2.04 Å). Li1–O1 and Li4–O4 interactions are relatively long (mean Li–O 2.29 Å) and contrast with Li2–O1 and Li3–O4 which are of intermediate length (mean 1.99 Å) and Li1–O2 and Li4–O3 which are short (mean 1.88 Å). Moreover, consistent with previous observations,[9] it is evidently the necessity for alkali metal stabilisation that imposes N-coordination on the core metal centres and incurs *Z*-configuration of these carboxylic amide ligands. Zincate anions represent the second ligand-type in **22**, their O-centres bridging between the two types of $\mathrm{Li^+}$ ion in the aggregate. These monoanions are analogous to those noted in **20**/**21**, with the combination of *E*-isomerism[22] and coordination of the $\mathrm{Zn(Bu^t)_2}$ moiety preventing the N-centres from replicating the coordinative behaviour noted for the N-lithiated carboxylic amide units. However, **22** reveals a larger C–Zn–C angle (mean 140.85°) than either **20** or **21**.



Scheme 3

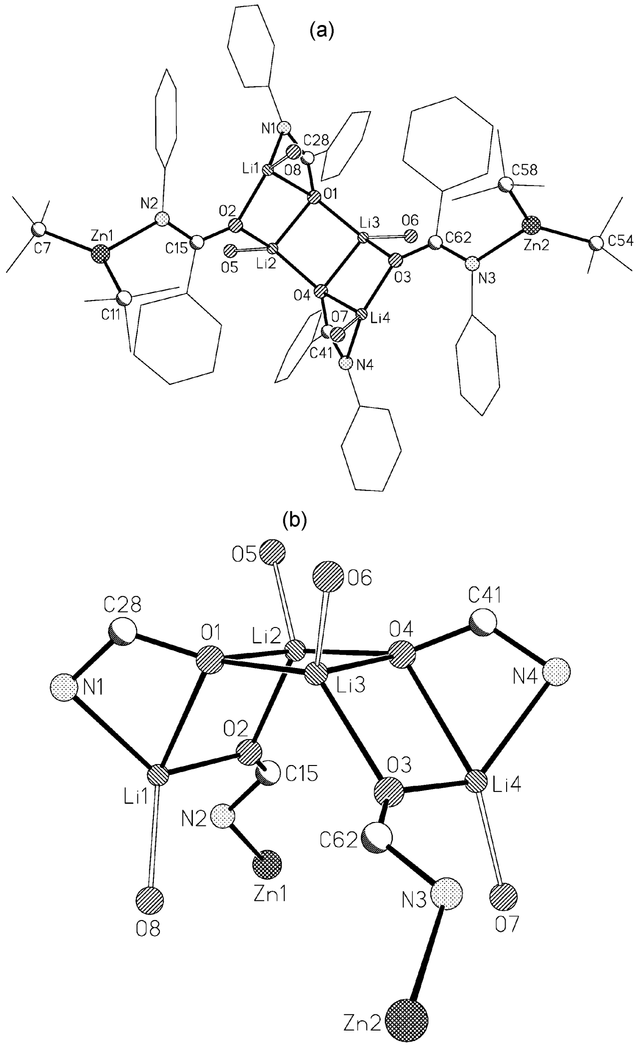


Fig. 6 (a) Structure of $\mathrm{(\textbf{22})_4{\cdot}5PhMe{\cdot}0.5thf}$; hydrogen atoms and lattice solvent molecules omitted and only the O-centres of coordinated thf shown. (b) Core of $\mathrm{(\textbf{22})_4{\cdot}5PhMe{\cdot}0.5thf}$.

Table 6 Selected bond lengths (Å), and angles (°) for $\mathrm{(\textbf{22})_4{\cdot}5PhMe{\cdot}0.5thf}$

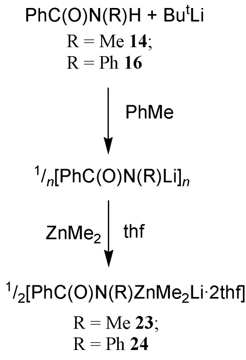
Li1–O2	1.883(13)	Zn2–N3	2.167(5)
Li2–O1	1.986(13)	Li1–N1	2.029(14)
Li3–O4	1.992(12)	Li4–N4	2.044(14)
Li4–O3	1.872(13)	N1–C28	1.296(9)
Li1–O1	2.326(15)	N4–C41	1.301(9)
Li3–O1	1.925(12)	O1–C28	1.293(7)
Li3–O3	1.984(12)	O4–C41	1.284(8)
Li2–O2	1.942(15)	O2–C15	1.284(9)
Li2–O4	1.914(12)	O3–C62	1.275(8)
Li4–O4	2.261(14)	N2–C15	1.315(10)
Zn1–N2	2.155(7)	N3–C62	1.325(8)
O1–Li1–O2	86.6(6)	Li1–O1–Li2	82.0(5)
O3–Li4–O4	88.2(5)	Li1–O1–C28	84.0(5)
O1–Li2–O2	95.3(6)	Li2–O1–Li3	88.1(5)
O3–Li3–O4	93.3(5)	Li3–O3–Li4	94.9(6)
O1–Li2–O4	92.0(5)	Li3–O4–Li4	83.6(5)
O1–Li3–O4	91.5(5)	Li4–O4–C41	84.3(5)
O1–Li1–N1	60.8(4)	Li2–O4–Li3	88.2(5)
O4–Li4–N4	62.2(4)	C7–Zn1–C11	142.0(5)
Li1–O2–Li2	95.9(6)	C54–Zn2–C58	139.7(3)

Formally N-lithiated carboxylic amides have hitherto been fully characterised only rarely. $\mathrm{[2\text{-}ArC(O)N(Bu^t)Li{\cdot}L]_{\mathit{n}}}$ [Ar = $\mathrm{(3\text{-}MeC_4H_2S)}$, L = *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine (pmdeta), *n* = 1; Ar = $\mathrm{C_5H_4N}$, L = hexamethylphosphoramide (hmpa), *n* = 2] reveal no interactions between the formally deprotonated N-centre and the metal.[22] Intramonomer N,O-chelation of the type seen in **22** has been noted in $\mathrm{[PhC(O)N(Pr^i)Li]_6{\cdot}2thf}$,[17] $\mathrm{[Bu^nC(O)N(Bu^t)Li]_6}$[25] and $\mathrm{[PhC(O)N(Pr^i)Li]_8}$.[26] However, whereas thf-solvation causes two of the amide moieties in $\mathrm{[PhC(O)N(Pr^i)Li]_6{\cdot}2thf}$ to adopt (non-chelating) *Z*-configurations,[17] those in **22** retain both N-coordination and *E*-configuration in spite of the presence of external donor. The close similarity between zincate anion geometries in **20**–**22** suggests that the last of these species can be viewed as a co-complex between a lithium zincate and another metallo-organic species (an N-lithio carboxylic amide) which is (conceptually) generated by the formation *in situ* of two molecules of $\mathrm{Zn(Bu^t)_2}$. To the best of our knowledge this is the first time that a co-complex such as this has been fully characterised. Both the lithium carboxylic amide and the lithium zincate components of **22** reveal a similar degree of azaenolate character to that noted in **20** and **21**, suggesting the retention of significant carbonylic character in the organic fragment. This contrasts with three of the five previously characterised N-deprotonated lithium carboxylic amides, with only $\mathrm{[ArC(O)N(Bu^t)Li{\cdot}L]_{\mathit{n}}}$ revealing a like trend.

Complex **22** also provides a structural model for the interaction of a lithium zincate dimer (of, say, **20**) with an N-lithio carboxylic amide dimer based on a Li2O4Li3O1 metallocycle. Coordination of the carboxylic amide N-centres (N1/4) to the zincate alkali metal centres (Li1/4) can be viewed as having incurred cleavage of the lithium zincate dimer at Li1–O3 and Li4–O2 (Fig. 6(b)). With respect to the orientations of the aza-enolate backbones in each zincate ligand (compare Fig. 4 with Fig. 6(a)) the bonds that have been broken correspond to the longer lithium-oxygen bonds in the core of the dimer of **20**. The result is to afford the non-bonding lithium–oxygen fragments in **22** and to introduce the last noteworthy feature of this co-complex: it incorporates a structural core that reveals both ladder and "open" pseudo cubane characteristics. Hence, rather than pertaining to a straightforward, chair-shaped $(LiO)_4$ ladder structure,[9,16] **22** reveals a boat-shaped array of edge-fused $(LiO)_2$ rings. In this sense it is related to the pseudo-cubane structure-type commonly seen for a wide variety of lithiated organics (*viz.* alkoxides etc.).[15] While the observation of non-bonding Li1 ··· O3 and Li4 ··· O2 distances (4.494 and 4.395 Å, respectively) suggest that **22** could be described as having an "open" pseudo-cubic core in which two *trans* edges of a single face have cleaved, it should be recognised that the only precedent for such a structure-type—the alkoxide $[(2\text{-MeO})C_6H_4C(H)(NMeCH_2CH_2NMe_2)OLi]_4$—revealed significantly shorter Li ··· O non-bonding distances (mean 2.723 Å).[15] Nevertheless, the long non-bonding Li ··· O distances in **22**, when considered in light of the recent structural characterisation of lithium aluminate $[PhC(O)N(Me)Al(Me)(Bu^t)OMe]\text{-}Li\cdot\{PhC(O)N(Me)Al(Me)[O(Bu^t)]OMe\}Li$,[9] suggest that $(LiO)_4$-based alkali metal 'ate systems will reveal some tendency for ladder formation.

The observation of $Zn(Bu^t)_2$ moieties in **20**–**22** raises questions about the mechanism which operates in these systems. The isolation of **17**–**19** from the 1 : 1 reactions of $ZnMe_2$ with the appropriate carboxylic amide points to the subsequent formation of **20**–**22** from zinc monoamide precursors rather than the diamides $Zn[N(R)C(O)Ph]_2$. However, the observation that **17**–**19** combine with equimolar Bu^tLi to afford $PhC(O)N(R)Zn(Bu^t)_2Li\cdot n\text{thf}$ rather than $PhC(O)N(R)Zn(Bu^t)MeLi\cdot n\text{thf}$ indicates the non-trivial attack of Bu^tLi. Moreover, it contrasts with the previously noted and straightforward reaction of Bu^tLi with related dimethylaluminium substrates.[9] Lastly, the length of Zn–N interactions in **20**–**22** [range 2.078(3)–2.184(4) Å] relative to analogous interactions [range 2.010(4)–2.050(3) Å] in **17**–**19** suggests the instability of certain zincates with respect to dialkylzinc evolution and, conceivably, formation of the lithium carboxylic amide units in **22**.

The straightforward 1 : 1 : 1 reaction of PhC(O)N(R)H, Bu^tLi and $ZnMe_2$ has been achieved by combining reagents *in that order* (Scheme 4). The lithiation of PhC(O)N(R)H (R = Me **14**, Ph **16**) with Bu^tLi can be followed by treatment of the resultant slurry with $ZnMe_2$ to yield products which ^1H NMR spectroscopy suggests to be lithium zincates of the type $PhC(O)N(R)ZnMe_2Li\cdot 2\text{thf}$ (R = Me **23**, Ph **24**).



Scheme 4

Table 7 Selected bond lengths (Å) and angles (°) for **24**

Li1–O1	1.917(5)	Li2–O6	1.962(5)
Li1–O2	1.975(5)	Zn1–N1	2.135(2)
Li1–O3	1.993(5)	Zn2–N2	2.144(2)
Li1–O4	1.972(5)	C9–O1	1.275(3)
Li2–O1	1.966(5)	C9–N1	1.308(3)
Li2–O2	1.933(5)	C24–O2	1.278(3)
Li2–O5	1.967(5)	C24–N2	1.306(3)
O1–Li1–O2	88.21(19)	Li1–O2–Li2	91.30(19)
O1–Li2–O2	88.40(19)	C1–Zn1–C2	144.74(12)
Li1–O1–Li2	92.1(2)	C16–Zn2–C17	145.38(16)

The structure of **22** implies the evolution of dialkylzinc from a tetrameric zincate precursor—a view reinforced by the observation that upon isolation from mother liquor, **23** fumes in an inert atmosphere. Consequently this last complex could not be fully (X-ray) characterised. However, the employment of benzanilide in place of **14** afforded $PhC(O)N(Ph)ZnMe_2Li\cdot 2\text{thf}$ **24**, the single crystal structure of which could be elucidated. In the solid state it reveals a dimer (Fig. 7, Table 7) isostructural with those noted for **20**/**21** with the organic ligands residing at 113.7° to each other. The Zn–N bond in **24** (mean 2.140 Å) lies within the range described by those in **20**–**22** [*cf.* mean 2.089 Å (**20**), 2.184 Å (**21**), 2.161 Å (**22**)]. As for **22**, the length of this bond relative to analogous interactions in **17**–**19** is suggestive of the instability of **23** towards $ZnMe_2$ evolution. Moreover, for **20**–**22** and **24** a correlation is observed between Zn–N bond lengths and C–Zn–C angles. Consistent with the presence of smaller zinc-bonded organic residues (that is, with the diminishment of steric interference between N-bonded and Zn-bonded groups), the C–Zn–C angles in **24** are larger than those in **20**–**22**. Hence, the mean C–Zn–C angle of 145.06° in **24** is significantly greater than the corresponding means of 136.89° in **20**, 132.29(16)° in **21**, and 140.85° in **22**. Moreover, the C–Zn–C angle in **24** is significantly more massive than that of 131.64(13)° noted recently in the triimidosulfonate $MeS(NBu^t)_2N(Bu^t)ZnMe_2Li\cdot 2\text{thf}$ [wherein Zn–N = 2.1374(17) Å].[27]

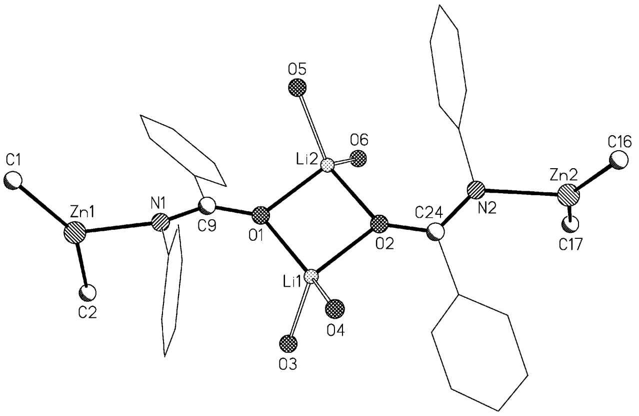


Fig. 7 Structure of $(\mathbf{24})_2$; hydrogen atoms omitted and only the O-centres of coordinated thf shown.

Lastly, the synthesis and isolation of **23**/**24**, when taken in conjunction with the observed instability of the former complex and the observation of PhC(O)NLi moieties in **22**, suggests the intriguing possibility that a Lewis acid (ZnR_2) can act as a solvent to deaggregate a lithiated organic {in this case $[PhC(O)N(R)Li\cdot 2\text{thf}]_n$} by coordinating the negative charge centre. Whereas repeated attempts to generate and isolate the *N*-isopropyl congener of **23**/**24** were unsuccessful, it seems likely that the sequential treatment of $PhC(O)N(Pr^i)H$ **15** with Bu^tLi, $ZnMe_2$ and thf should yield a dimer analogous to that of **24** in the solid state. This contrasts with the observation that $[PhC(O)N(Pr^i)Li]_8$[26] is deaggregated only to $[PhC(O)N(Pr^i)Li]_6\cdot 2\text{thf}$[17] in the presence of excess Lewis base. With this in mind, attempts to mimic the synthesis of **22** by the 2 : 2 : 1 reaction of benzanilide, Bu^tLi and $ZnMe_2$ are ongoing, though so far have afforded only **24** in depleted yield.

Conclusions

The isolation and characterisation of **17**–**19** provides us with some understanding of the associative behaviour and structural chemistry of formally N-zincated carboxylic amides, while that of **20**–**24** has afforded new insights into lithium zincate stability and chemistry and, for **22**, the unexplored field of co-complex formation between lithium zincates and other potentially reactive molecules. However, the processes which convert **17**–**19** into **20**–**22** are plainly non-trivial and, in this context, the straightforward preparation of $[PhC(O)N(R)ZnMe_2]^-$ ions (**23**/**24**) is noteworthy. The synthetic pathways to **20**–**22**, along with the stabilities (with respect to dialkylzinc emission) and reactivities of such complexes, are the subject of ongoing study. Combining these two approaches, attempts are being made to generate further examples of lithium zincate-incorporating co-complexes both utilising the route which affords **22** and also by investigating the receptivity of lithiated organics to treatment with a deficiency of diorganozinc Lewis acids. The solution behaviour of **20**–**22** and **24** is being probed with a view to understanding whether the evident ability of certain lithium zincates to emit dialkylzinc has ramifications for our view of the form which so-called "'ate complexes" take in solution and whether we might more generally view Lewis acid molecules as potential stabilisers of the negative charge centres in lithiated organics.

Experimental

Methods and materials

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard double manifold and glove-box techniques. Chemical reagents were used as received from Aldrich without further purification. *N*-isopropyl benzamide **15** was synthesised according to a literature procedure.[17] Toluene, hexane and thf were distilled off sodium or sodium-potassium amalgam immediately prior to use.

NMR data were collected on either a Bruker DPX 400 or DRX 400 (400.12 MHz for ^1H and and 100.03 for ^{13}C) or a Bruker DRX 500 FT NMR spectrometer (500.05 MHz for ^1H and 125.01 for ^{13}C) at 27 °C. Chemical shifts are internally referenced to deuterated solvents and calculated relative to TMS.

Synthesis and characterisation

$[PhC(O)N(ZnMe)Me]_6\cdot 2PhMe$ $(17)_6\cdot 2PhMe$. $ZnMe_2$ (0.5 ml, 1 mmol, 2.0 M in toluene) was added to a solution of *N*-methyl benzamide (**14**, 0.14 g, 1 mmol) in toluene (1 ml). The resultant colourless solution was stored at +5 °C for 24 h to yield crystals of $(17)_6\cdot 2PhMe$. Yield 212 mg (87%), mp 192–194 °C. Found: C 51.57, H 5.19, N 5.85%. Calc. for $C_{68}H_{82}N_6O_6Zn_6$: C 52.01, H 5.77, N 5.87%. ^1H NMR (400 MHz, $[^2H_6]$benzene), δ 7.62 (dd, 2H, Ph), 7.21–7.13 (m, 4H, Ph + *Ph*Me), 2.85 (s, 3H, NMe), 2.19 (s, 0.8H, Ph*Me*), −0.37 (s, 3H, ZnMe). ^{13}C NMR (100 MHz, $[^2H_6]$benzene), δ 176.3 (CO), 135.1 (*i*-Ph), 130.7, 129.1, 128.6, 126.5, 125.4 (*o*-, *m*-Ph + *Ph*Me), 38.0 (NMe), 21.4 (Ph*Me*), −17.4 (ZnMe).

$[PhC(O)N(ZnMe)(Pr^i)]_4$ $(18)_4$. A solution of *N*-isopropyl benzamide[17] (**15**, 0.16 g, 1 mmol) in toluene (1 ml) was treated with $ZnMe_2$ (0.5 ml, 1 mmol, 2.0 M in toluene). The colourless solution which resulted was reduced to half volume and hexane (0.25 ml) was added. Storage at −30 °C for 24 h afforded crystals of $(18)_4$. Yield 42 mg [17%; this increases to 200 mg (82%) of amorphous material which analyses as $(18)_4$ if the reaction is reduced to dryness], mp 116–118 °C. Found: C 54.01, H 6.56, N 4.78%. Calc. for $C_{44}H_{60}N_4O_4Zn_4$: C 54.45, H 6.23, N 5.77%. ^1H NMR spectroscopy (400 MHz, $[^2H_6]$benzene), δ 7.81–7.79 (m, 2H, Ph), 7.21–7.06 (m, 3H, Ph), 3.88 (sept., 1H, C*H*Me), 1.26 (d, 3H, CH*Me*), 1.06 (d, 3H, CH*Me*), −0.32 (s, 3H, ZnMe). ^{13}C NMR (400 MHz, $[^2H_6]$benzene), δ 174.4 (CO), 135.4 (*i*-Ph), 130.3, 128.7, 128.1 (*o*-, *m*-Ph), 51.0 (*C*HMe), 24.6, 23.9 (CH*Me*), −11.5 (ZnMe).

$[PhC(O)N(ZnMe)Ph]_4\cdot 2PhMe$ $(19)_4\cdot 2PhMe$. $ZnMe_2$ (0.5 ml, 1 mmol, 2.0 M in toluene) was added to a solution of benzanilide (**16**, 0.20 g, 1 mmol) in toluene (1 ml). The colourless solution which formed was treated with further toluene (4 ml) and stored at room temperature for 24 h to yield crystalline $(19)_4\cdot 2PhMe$. Yield 183 mg (57%), mp 246–248 °C. Found: C 64.46, H 5.21, N 4.43%. Calc. for $C_{70}H_{68}N_4O_4Zn_4$: C 65.13, H 5.31, N 4.34%. ^1H NMR (400 MHz, $[^2H_6]$benzene), δ 7.73 (dd, 2H, Ph), 7.10–6.79 (m, 7H, Ph + *Ph*Me), 6.56 (d, 2H, Ph), 2.19 (s, 0.8H; Ph*Me*), −0.13 (s, 3H, ZnMe). ^{13}C NMR (400 MHz, $[^2H_6]$benzene), δ 175.4 (CO), 147.2, 134.5 (*i*-Ph), 131.9, 131.3, 129.3, 125.6, 125.1, 124.7 (*o*-, *m*-Ph + *Ph*Me), 21.4 (Ph*Me*), −15.1 (ZnMe).

$PhC(O)N(Me)Zn(Bu^t)_2Li\cdot 2thf\cdot 0.5PhMe$ $(20)_2\cdot PhMe$. N-Methyl benzamide **14** (0.14 g, 1 mmol) in toluene (2 ml) was treated with $ZnMe_2$ (0.5 ml, 1 mmol, 2.0 M in toluene). The mixture was refluxed and then cooled to −78 °C whereupon Bu^tLi (0.59 ml, 1 mmol, 1.7 M in pentane) was added and the resultant suspension allowed to warm to room temperature. Dissolution was effected by adding thf (1 ml). Reduction to half-volume, followed by storage at −30 °C for 2 days yielded needles of $(20)_2\cdot PhMe$. Yield 71 mg (28% by Bu^tLi), mp 120–122 °C. Found: C 61.96, H 8.71, N 2.89%. Calc. for $C_{55}H_{92}Li_2N_2O_6Zn_2$: C 64.64, H 9.07, N 2.74%. ^1H NMR (500 MHz, $[^2H_8]$thf), δ 7.67 (m, br, 4H, Ph), 7.27 (m, br, 6H, Ph), 7.20–7.10 (m, 5H, *Ph*Me), 3.62 (m, 12H, thf), 2.30 (s, 3H, Ph*Me*), 1.78 (m, 12H, thf), 0.81 (s, 36H, Bu^t). ^{13}C NMR (125 MHz, $[^2H_8]$thf), δ 138.4, 129.6, 128.9, 128.6, 127.4, 126.0 (Ph + *Ph*Me), 68.2 (thf), 34.4 (Bu^t), 26.4 (thf), 22.4 (Ph*Me*).

$PhC(O)N(Pr^i)Zn(Bu^t)_2Li\cdot 2thf$ 21. $ZnMe_2$ (0.5 ml, 1 mmol, 2M in toluene) was added to a slurry of *N*-isopropyl benzamide **15** (0.14 g, 1 mmol) in toluene (2 ml). The resultant solution was cooled to −78 °C whereupon Bu^tLi (0.59 ml, 1 mmol, 1.7 M in pentane) was added and the resultant suspension allowed to warm to room temperature. The addition of thf (0.2 ml) afforded a yellow solution. Reduction to half-volume, followed by storage at −30 °C for 2 days yielded blocks of **21**. Yield 88 mg (36% by Bu^tLi), mp 108–110 °C. Found: C 62.61, H 9.04, N 3.18%. Calc. for $C_{26}H_{46}LiNO_3Zn$: C 63.35, H 9.41, N 2.84%. ^1H NMR (500 MHz, $[^2H_8]$thf), δ 7.59–7.05 (m, 6.2H, Ph + *Ph*Me), 4.14 (m, br, 1H, C*H*Me_2), 3.59 (m, 4H, thf), 2.28 (s, H, Ph*Me*), 1.75 (m, 4H, thf), 1.17 (d, 6H, CH*Me*), 0.75 (s, 18H, Bu^t). ^{13}C NMR (125 MHz, $[^2H_8]$thf), δ 145.4 (*i*-Ph), 138.4 (*i*-*Ph*Me), 129.7, 128.9, 128.7, 127.3, 126.0 (Ph + *Ph*Me), 68.2 (thf), 46.2 (NCH), 34.6 (Bu^t), 26.4 (thf), 24.0 (br, CH*Me*), 21.4 (Ph*Me*).

$\{[PhC(O)N(Ph)Li\cdot thf]\cdot[PhC(O)N(Ph)Zn(Bu^t)_2Li\cdot thf]\}_4\cdot 5PhMe\cdot 0.5thf$ $(22)_4\cdot 5PhMe\cdot 0.5thf$. $ZnMe_2$ (0.5 ml, 1 mmol, 2.0 M in toluene) was added to benzanilide **16** (0.20 g, 1 mmol) in toluene (2 ml). After refluxing, the mixture was reacted with Bu^tLi (0.59 ml, 1 mmol, 1.7 M in pentane) at −78 °C and the resultant suspension was allowed to warm to room temperature. The addition of thf (0.4 ml) afforded a solution which was reduced to half-volume and stored at −30 °C for 2 days to give $(22)_4\cdot 5PhMe\cdot 0.5thf$. Yield 74 mg [35% by Bu^tLi assuming $Zn(Bu^t)_2$ elimination (see text)], mp decomp. 128–130 °C (loses solvent from 95 °C). Found: C 66.10, H 7.91, N 3.10%. Calc. for $C_{173}H_{224}Li_8N_8O_{16}Zn_4$: C 69.52, H 7.55, N 3.75%. ^1H NMR (400 MHz, $[^2H_8]$thf), δ 7.85–6.77 (m, 21H, Ph + *Ph*Me), 3.59 (m,

Table 8 Crystallographic data for **(17)**$_6$·2PhMe, **(18)**$_4$, **(19)**$_4$·2PhMe, **(20)**$_2$·PhMe, **21**, **(22)**$_4$·5PhMe·0.5thf and **(24)**$_2$ (Mo-Kα radiation, $\lambda = 0.71069$ Å)

	(17)$_6$·2PhMe	**(18)**$_4$	**(19)**$_4$·2PhMe	**(20)**$_2$·PhMe	**21**	**(22)**$_4$·5PhMe·0.5thf	**(24)**$_2$
Formula	$C_{68}H_{82}N_6O_6Zn_6$	$C_{44}H_{60}N_4O_4Zn_4$	$C_{70}H_{68}N_4O_4Zn_4$	$C_{55}H_{92}Li_2N_2O_6Zn_2$	$C_{26}H_{46}LiNO_3Zn$	$C_{205}H_{260}Li_8N_8O_{16.5}Zn_4$	$C_{46}H_{64}Li_2N_2O_6Zn_2$
M_r	1471.62	970.44	1290.76	1021.93	492.95	3417.21	885.61
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1$	$P2_1/c$	$P2_1/n$	$Ccca$	$P\bar{1}$	$P2_1/c$
a/Å	12.7129(5)	12.3508(4)	17.8227(3)	15.0541(3)	17.2883(4)	21.937(4)	12.915(3)
b/Å	13.6902(7)	13.6939(5)	14.8838(3)	17.0524(4)	18.7603(6)	24.142(5)	14.378(3)
c/Å	19.6809(9)	14.9131(5)	24.9876(3)	23.7500(5)	17.5158(6)	24.510(5)	26.365(5)
α/°	90	90	90	90	90	72.69(3)	90
β/°	108.571(2)	98.445(2)	108.6810(10)	96.626(2)	90	87.39(3)	103.58(3)
γ/°	90	90	90	90	90	64.56(3)	90
U/Å^3	3246.9(3)	2494.91(15)	6279.24(18)	6056.1(2)	5681.0(3)	11140(4)	4758.9(17)
Z	2	2	4	4	8	2	4
D_c/g cm^{-3}	1.505	1.292	1.365	1.121	1.153	1.005	1.236
μ/mm^{-1}	2.231	1.954	1.560	0.835	0.888	0.478	1.053
T/K	180(2)	180(2)	180(2)	180(2)	180(2)	230(2)	180(2)
Measured reflections	10939	14279	53726	41988	22386	51528	34594
Unique reflections	3171	9412	14308	13617	3258	26805	10458
R_{int}	0.0280	0.0346	0.0358	0.0615	0.0412	0.0568	0.0432
Final $R(F)$, $wR(F^2)$	0.0350, 0.1026	0.0383, 0.0799	0.0504, 0.1464	0.0673, 0.1835	0.0528, 0.1149	0.0949, 0.2991	0.0451, 0.1189
Parameters	335	505	655	760	221	1939	527
GoF	0.943	1.028	1.016	1.018	1.091	1.030	1.070
Max. peak, hole/e Å^{-3})	0.76, −0.60	0.36, −0.37	0.84, −0.66	0.78, −0.62	0.43, −0.95	0.61, −0.56	0.47, −0.48

8H, thf), 2.28 (s, 0.5H, Ph*Me*), 1.75 (m, 8H, thf), 0.72 (s, 18H, Bu^t). ^{13}C NMR (100 MHz, [^{2}H$_8$]thf), δ 152.8, 144.5 (*i*-Ph), 129.6, 129.3, 128.9, 128.4, 128.1, 126.0, 125.6, 121.3 (Ph + *Ph*Me), 68.2 (thf), 34.6 (Bu^t), 26.4 (thf), 22.5 (Ph*Me*).

PhC(O)N(Me)ZnMe$_2$Li·2thf 23. A suspension of *N*-methyl benzamide **14** (0.14 g, 1 mmol) in toluene (0.75 ml) was reacted with Bu^{t}Li (0.59 ml, 1 mmol, 1.7 M in pentane) at −78 °C. The resultant mixture was allowed to warm to room temperature, whereupon the addition of ZnMe$_2$ (0.5 ml, 1 mmol, 2.0 M in toluene) afforded a pale yellow suspension with the addition of thf (0.2 ml) yielding a yellow solution. Storage at −30 °C for 2 days gave **23**. Yield 156 mg (41%), mp 88–90 °C. Found: C 57.84, H 7.85, N 3.14%. Calc. for $C_{18}H_{30}LiNO_3Zn$: C 56.78, H 7.94, N 3.68%. ^{1}H NMR (400 MHz, [^{2}H$_8$]thf), δ 7.67–7.64 (m, 2H, Ph), 7.25–7.15 (m, 3H, Ph), 3.63 (m, 7H, thf), 2.86 (s, 3H, NMe), 1.79 (m, 7H, thf), −1.17 (s, 6H, ZnMe). ^{13}C NMR (100 MHz, [^{2}H$_8$]thf), δ 172.4 (CO), 144.4 (*i*-Ph), 129.6, 128.9, 128.6, 128.2, 128.0, 126.0 (Ph), 68.2 (thf), 32.4 (NMe), 26.4 (thf), −10.4 (ZnMe).

PhC(O)N(Ph)ZnMe$_2$Li·2thf 24. A suspension of benzanilide **16** (0.20 g, 1 mmol) in toluene (0.75 ml) was reacted with Bu^{t}Li (0.59 ml, 1 mmol, 1.7 M in pentane) at −78 °C. The mixture was allowed to warm to room temperature and ZnMe$_2$ (0.5 ml, 1 mmol, 2.0 M in toluene) was added to give a pale yellow suspension. Treatment with thf (0.2 ml) yielded a solution from which **24** deposited after 2 days at −30 °C. Yield 300 mg (67%), mp 68–70 °C. Found: C 63.14, H 7.21, N 3.35%. Calc. for $C_{23}H_{32}LiNO_3Zn$: C 62.38, H 7.28, N 3.16%. ^{1}H NMR (400 MHz, [^{2}H$_6$]benzene), δ 7.57–6.86 (m, 11H, Ph + *Ph*Me), 3.60 (m, 8H, thf), 2.20 (s, 1H, Ph*Me*), 1.46 (m, 8H, thf), −0.54 (s, 6H, ZnMe). ^{13}C NMR (100 MHz, [^{2}H$_6$]benzene), δ 129.1, 128.5, 128.4, 125.4, 124.3, 121.8 (Ph + *Ph*Me), 67.6 (thf), 21.0 (Ph*Me*), 25.5 (thf), −7.2 (ZnMe). ^{1}H NMR (400 MHz, [^{2}H$_8$]thf), δ 7.96 (br, 2H, Ph), 7.26–7.10 (m, 9H, Ph + *Ph*Me), 6.51 (br, 1H, Ph), 3.63 (m, 7H, thf), 2.32 (s, 1H, Ph*Me*), 1.79 (m, 7H, thf), −1.04 (s, 6H, ZnMe). ^{13}C NMR (100 MHz, [^{2}H$_8$]thf), δ 168.8 (CO), 152.8, 144.3 (*i*-Ph), 138.3, 129.7, 129.6, 128.8, 128.7, 128.5, 128.3, 127.9, 125.9, 125.7, 121.0 (Ph + *Ph*Me), 68.1, 26.3 (thf), 21.4 (Ph*Me*), −10.0 (ZnMe).

X-Ray crystallography

Crystallographic data (excluding structure factors) for **(17)**$_6$·2PhMe, **(18)**$_4$,**(19)**$_4$·2PhMe, **(20)**$_2$·PhMe, **21**, **(22)**$_4$·5PhMe·0.5thf and **24** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications Data were collected using a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device (Table 8). Structures were solved by direct methods[28] and refined against F^2 using SHELXL-97[29] [for **(17)**$_6$·2PhMe, **21** and **24**] or SHELXTL NT 5.10[30] [for **(22)**$_4$·5PhMe·0.5thf].

For all structures, hydrogen atoms were placed geometrically and allowed to ride during subsequent refinement. The phenyl rings in **(22)**$_4$·5PhMe·0.5thf were refined as rigid groups and thf ligands were refined with restraints on the C–C distances. The O-centre in the lattice thf molecule could not be identified and the ring atoms were all refined as carbon.

CCDC reference numbers 167401, 167402 and 184194–184198.

See http://www.rsc.org/suppdata/dt/b2/b210479b/ for crystallographic data in CIF or other electronic format.

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