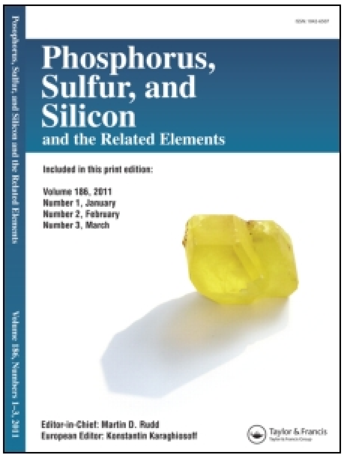

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Selective Oxygen Capture in Lithium Zincate Chemistry

DAVID J. LINTON, ROBERT P. DAVIES, PAUL SCHOOLER
and ANDREW E. H. WHEATLEY

*Cambridge University Chemical Laboratories Lensfield Road,
Cambridge CB2 4EW, U.K.*

Sequential reaction of N=C-N-containing ligands with $ZnMe_2$, ^tBuLi, pre-dried (P_2O_5) air and tetrahydrofuran affords crystalline species which demonstrate differing modes of oxo-capture. Whereas oxo-insertion into a metal-carbon bond is implicated for L = (2-Pyr)N(H)Ph (Pyr = pyridyl) and PhNC(Ph)N(H)Ph, when L = (2-Pyr)N(H)Bz (Bz = benzyl) ^tBuOLi co-crystallises with the tetrahedral oxo-encapsulation complex, $(\mu_4\text{-}O)Zn_4[(2\text{-}Pyr)NBz]_6$ 2. For L = (2-Pyr)N(H)Me the only isolable product of reaction is the novel octahedral complex $^tBu(\mu_3\text{-}O)Li_3(\mu_6\text{-}O)Zn_3[(2\text{-}Pyr)NMe]_6$, 3, which demonstrates both encapsulation of oxygen and insertion into metal-carbon bonds.

Keywords: lithium; zinc; oxygen; encapsulation; solid-state structure

While organolithium reagents perform 1,2-addition across α,β-unsaturated ketones, it has been reported lately that in the presence of Group 13 Lewis acids 1,4-addition is preferred.[1] Conjugate addition is also incurred by the use of lithium triorganozincate species, and these reagents are receiving increased attention by virtue of their ability to effect chemical transformations whose selectivities differ from those observed for other organometallic compounds.[2,3] In spite of this, the structural chemistry of lithium zincates is not well understood.

In the light of recent advances in the controlled oxygenation of heterobimetallic compounds,[4] and following on from previous work in which closely bidentate amine ligands of the form $R-N=C(R')-N(H)-R''$ were used to stabilise unusual metal aggregates,[5] we set out to investigate the structural chemistry of lithium zincates with particular regard to their behaviour upon oxygenation.

Reaction of $ZnMe_2$ with (2-Pyr)N(H)Ph, followed by addition of ${}^tBuLi$ and treatment with dry (P_2O_5) air, yielded a complex which was shown by X-ray crystallography to be the dimeric compound $\{LiO(Me)Zn[(2\text{-}Pyr)NPh]_2\}_2\cdot 2THF$, **1**. This is a THF-solvated lithium triorganozincate in which the zinc centre achieves tetracoordination through dimerisation. Treatment of the reaction mixture with oxygen can be viewed as having effected the insertion of oxygen atoms either into Zn–Me bonds or, alternatively, into *in situ* generated MeLi.

When the amidine, PHNC(Ph)N(H)Ph, is substituted for (2-Pyr)N(H)Ph in the reaction, the only isolable product was the complex $[{}^tBu(\mu_3\text{-}O)]_2LiZn_2[PhNC(Ph)NPh]_3$, **4**, in which a triangular, non-bonded arrangement of metal centres is capped on either side by an O^tBu group. Here, then, oxo-insertion has empirically occurred into Li–C bonds, with concomitant coordination by an amidinozinc species.

When the reaction is performed with (2-Pyr)N(H)Bz, two separate modes of behaviour are observed: while ^1H NMR spectroscopy demonstrates that one of the two isolable crystalline products is the simple oxo-*insertion* product ${}^tBuOLi$, the other is **2**, $(\mu_4\text{-}O)Zn_4[(2\text{-}Pyr)NBz]_6$, which incorporates an oxo-*encapsulating* Zn_4 motif. The six aminopyridine ligands in **2** each use their N–C=N groups to bridge one non-bonding edge of the Zn_4 tetrahedron, so that Zn(2) (FIGURE 1, left) is coordinated by three pyridyl N-centres, whereas the other three Zn ions are each bonded to one pyridyl and two deprotonated N-centres.

The two modes of oxygen capture are combined in a single molecule when (2-Pyr)N(H)Me is employed in the same reaction. X-ray studies show that the product of oxygenation is ${}^{t}\mathrm{Bu}(\mu_3\text{-O})\mathrm{Li}_3(\mu_6\text{-O})\mathrm{Zn}_3[(2\text{-Pyr})\mathrm{NMe}]_6$, **3**, the solid-state structure of which is based on an oxo-encapsulating, *fac*-isomeric $(\mu_6\text{-O})\mathrm{Li}_3\mathrm{Zn}_3$ octahedron with a face-capping $\mathrm{O}^{t}\mathrm{Bu}$ group (FIGURE 1, right).

An $\mathrm{M}_3\mathrm{M}'_3$ environment at oxygen has not previously been observed, although metal clusters incorporating $(\mu_6\text{-O})$ are well known, particularly in the chemistry of lithium where several homometallic $(\mu_6\text{-O})$ species have been characterised.[6] Several $(\mu_6\text{-O})\mathrm{M}_2\mathrm{M}'_4$ clusters have been prepared,[7,8] whilst a compound with MM'_5 stoichiometry has also been reported.[9] Further, all of the published mixed s/p-block and transition metal μ_6-O-based structures also feature single, edge-[7] or face-bridging[8] donor atoms.

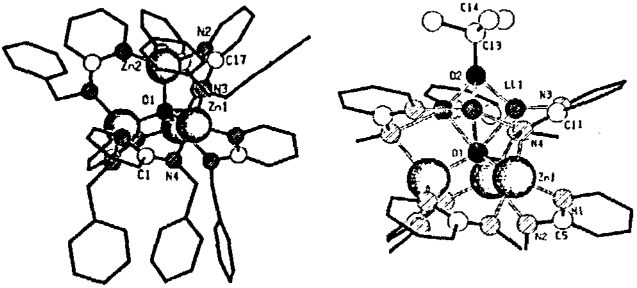

FIGURE 1. The structures of **2** (left) and **3**. Hydrogen atoms omitted for clarity.

The structures of **2** and **3** show several intriguing similarities, apart from the simple encapsulation of an O^{2-} ion. The basal $\mathrm{Zn}_3[(2\text{-Pyr})\mathrm{NR}]_3$ tier is almost identical in the two structures. Moreover, the remaining three aminopyridine ligands also bond in a very similar way—the pyridyl N-centres donate lone-pair electron density to the upper metal fragment in both cases, with the deprotonated N-centres bonding to the (lower) Zn_3 fragment. In **2**, however, these N-centres do not bond to the apical ion in the way that their analogues are observed to bond to Li in **3**. The difference is due to the fact that the ligands in **2** lie at a greater angle to the basal tier; this arching over of the ligands places the apical Zn centre in an approximately tetrahedral environment.

Thus, in **3** and **2** the $[\mathrm{O}\{\mathrm{Zn}[(2\text{-Pyr})\mathrm{NR}]_2\}_3]^{2-}$ group can be viewed as an inorganic, tetradentate ligand, where coordination of a triangular (3) or spherical (2) metal fragment to the O-centre is augmented by donation from free pyridyl groups. In 3, the upper-tier metal fragment requires trigonal pyramidal coordination, whereas in 2 the unique Zn centre has a preference for tetrahedral coordination; in each case the aminopyridine ligands have the flexibility to provide the said metal fragment with the most favoured coordination sphere.

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