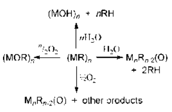
The oxygen scavenging properties of alkali metal-containing organometallic compounds



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Alkali metal-containing organometallic compounds are well known for their oxophilicity and, as a result, reactions utilising them must be carried out under an inert atmosphere with oxygen having to be scrupulously removed from the system if these complexes are to be successfully synthesised, manipulated or employed. Studies will be presented here which investigate the oxophilic nature of alkali metal-containing organometallic species. The route by which oxygen is scavenged from the environment will be considered, as will different effects to be had by varying the oxygen source. Discussion will focus primarily on the metal organo- and inorganooxide and oxide or peroxide coordination complex structural motifs which result from the reaction of oxophilic substrates.

1 Introduction

The reactivity of Group 1 organometallic compounds and Group 1-containing polymetallic compounds towards oxygen has been known for some time.[1] The result is that oxygen sources must be scrupulously removed from the reaction system not only during the preparation of such species, but also during their manifold synthetic applications. Nevertheless, reports exist in which the presence of trace oxygen has led to reaction of the organometallic oxophile. Isolation and structural characterisation of the resulting complexes have afforded us some understanding of the processes active during oxygen scavenging. In this context the chalcogen source is O_2 or H_2O and, as such, the majority of complexes discussed here will have been afforded by the reaction of an organometallic substrate with either of these sources.

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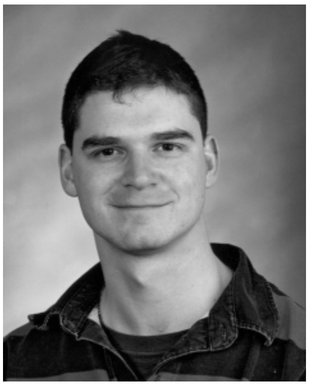

The compounds discussed here are ordered firstly by their metal components and secondly by the mode of chalcogen incorporation. The first part of this article deals with Group 1 metallated organics while the latter part deals with heteropolymetallic compounds. Each of these parts is further subdivided. Firstly, metal organo- and inorganooxides (yielded by the empirical insertion of an oxygen atom into a metal–carbon or metal–heteroatom bond, respectively) will be discussed. Secondly, the encapsulation of isolated chalcogenide dianions within homo- and heterometallic architectures will be presented. To aid the reader, the oxygen-incorporating compounds discussed here which form the basis of figures are identified as such at the point in the text where they are first allocated a number. However, before considering the structures of oxygen-incorporating species in detail it will serve to briefly discuss the mechanisms thought to be operative during what are, in effect, the controlled/partial oxidation and hydrolysis reactions of organometallic substrates.

1.1 Molecular oxygen

The reaction of alkali metal-containing organometallic substrates with molecular oxygen is well documented.[1] For homometallic species the process is thought to involve a radical chain decomposition in which, for lithiated organics, a peroxide intermediate degrades to an organooxide product. There is, however, a distinct paucity of structural data surrounding the species involved in such processes, with just one organoperoxide complex of lithium having been structurally characterised.[2]

1.2 Moisture

Whereas the partial hydrolysis of a Group 1 organometallic compound (MR) usually results in the formation of RH and MOH [eqn. (1)],[3] it has also been noted that such a process can yield the metal oxide [eqn. (2)]. Specifically, in the case of organolithium species, it has been noted that both LiOH and (more commonly) Li_2O can form co-complexes with unreacted organometallic, LiR.[4] It is worth pointing out that it is not uncommon to describe lithium oxide-containing clusters as co-complexes of the type $(LiR)_n{\cdot}Li_2O$. However, as the subsequent discussion will show, designation of the Li_2O fragment is almost always arbitrary for symmetry reasons. As a result, notation of the type $Li_{n+2}R_n(O)$ has been used in this review.

$$MR + H_2O \rightarrow H_2O \bullet MR \rightarrow RH + MOH \qquad (1)$$

$$(MR)_n + H_2O \rightarrow M_nR_{n-2}(O) + 2RH \qquad (2)$$

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2 Homometallic complexes

2.1 Metal organo- and inorganooxides

The insertion of oxygen into a metal–carbon bond in a homometallic complex has been noted in the mixed anion complex which results from the exposure of a LiO^tBu–hexane solution to *moist* air. The subsequently formed species, $(LiO^tBu)_{10}\cdot(LiOH)_6$ **1**, is a centrosymmetric dimer based on two hexagonal $Li_6(O^tBu)_5(OH)$ sub-aggregates which are joined by a tetrameric LiOH crossed-ladder. As the reader will observe, several of the complexes discussed in this review are thought to arise from either LiOH or Li_2O contamination of a commercial organolithium substrate. Hence, this compound is of particular note because of its implications for such 'pure' organolithium reagents. For example, the structure of **1** reveals that the incomplete hydrolysis of LiO^tBu affords not isolated conglomerates of hydrolysed and unhydrolysed materials but rather a mixed-anion co-complex which incorporates discrete domains of LiO^tBu and of LiOH. This cluster has been taken as a model for the incomplete hydrolysis of a lithium alkoxide.[3]

2.2 Metal oxides

Whereas several examples exist of μ_6-O^{2-} ions residing at the centre of an octahedral array of Group 1 metal centres (see below) all but one of these systems reveal a cage-like dicationic array that *encapsulates* the chalcogenide ion within an Li_nR_{n-2} shell. The exception to this rule lies in the product obtained by partial hydrolysis of the chiral pseudo-cubic dilithiate [HMPA-$\cdot Li_2$(salen)$]_2$ **2** [HMPA = hexamethylphosphoramide, salen = *N*,*N*′-ethylenebis(salicylideneimide)$^{2-}$]. Attempts to solubilize a suspension of $[Li_2(salen)]_n$ using TMEDA (rather than HMPA, TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) have been noted to be ineffectual. However, the subsequent dropwise addition of liquid H_2O results in complete dissolution, with a single, reproducible crystalline product being deposited from solution. X-Ray crystallography reveals this complex to be $H_2O\cdot(TMEDA)_2\cdot Li_8(salen)_3(O)$ **3** (Fig. 1), the formation of which implies the conversion of H_2O into Li_2O by an Li_2(salen) moiety with the alkali metal oxide thereafter being incorporated in the structure of **3**. In this aggregate, two distorted $(LiO)_4$ pseudo-cubanes are fused at a single O-centre surrounded by six Li^+ ions (mean Li–O = 1.883 Å) with each salen dianion contributing an oxygen centre to each pseudo-cubane.[5] The Li centres at the cubane vertices opposite the bridging oxide are each stabilised by three O-centres from three different salen dianions and by one monodentate TMEDA molecule—a highly unusual bonding mode for this normally bidentate Lewis base. Moreover, bearing in mind that only partial hydrolysis has occurred, it is surprising to note that *unreacted* water molecules reside in the crystal lattice. These form hydrogen bonds with the otherwise free TMEDA N-centres, affording infinite chains of **3** in the solid state.

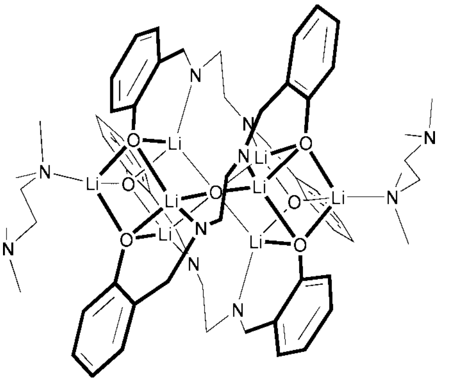


Fig. 1 $H_2O\cdot(TMEDA)_2\cdot Li_8(salen)_3(O)$ **3** is based on two oxygen-fused $(LiO)_4$ pseudo-cubanes.

X-Ray diffraction studies on the product obtained by the oxygen scavenging reaction of a primary lithium amide revealed the first μ_6-O^{2-} encapsulating lithium amide complex. Such a motif, with its octahedral Li_6O^{4+} core, is of particular interest because it represents a lipophilically-wrapped inorganic lattice fragment. Such a unit is, of course, insoluble in conventional organic solvents. However, an organic periphery will render such a lattice fragment more soluble and, thus, manageable. The reaction of Li^nBu with three equivalents of cyclopentylamine yielded a red solution at reflux, from which crystals of the precisely octahedral tetradecalithium complex $Li_{14}[N(H)(c\text{-}C_5H_9)]_{12}(O)$ **4** (Fig. 2) deposited on cooling [Li–(μ_6-O) = 1.888(10) Å].[6] The resultant cage compound, based as it is on a face-centred cubic array of tri-coordinate metal centres, is quite unlike the two-dimensional rings and ladders which dominate the field of lithium amide chemistry.[7] The synthesis of **4** was achieved in spite of adherence to standard Schlenk techniques and has been ascribed to the hygroscopic nature of the parent amine. In this context it has been noted that the employment of the triply distilled parent amine affords a yellow solution (*cf.* the red colour consistent with the preparation of **4**) from which material that analyses as the pure lithium amide, $[LiN(H)(c\text{-}C_5H_9)]_n$, is deposited.

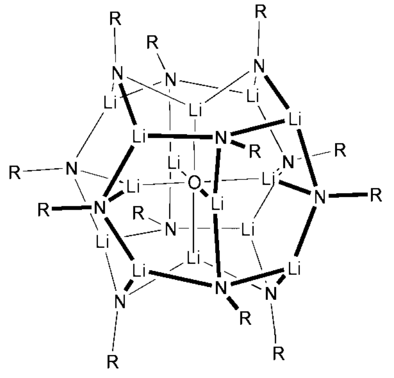


Fig. 2 Structure of $Li_{14}[N(H)R]_{12}(O)$ **4** (R = *c*-C_5H_9).

Whereas the synthesis of **4** employs an amine substrate, a similar pseudo-octahedral oxide encapsulation complex has been afforded by what is thought to be partial hydrolysis (though reaction with Li_2O contaminant in the commercial metallating agent cannot be ruled out) of the lithium amidinate dimer $\{Li[(N^tBu)_2C^nBu]\}_2$—a species which results from the nucleophilic addition of Li^nBu to 1,3-di-*tert*-butylcarbodiimide. The subsequently formed complex, $Li_6[(N^tBu)_2C^nBu]_4(O)$ **5** [eqn. (2), M = Li], reveals six-fold coordination of the oxide ion. It is rendered particularly unusual, in the context of oxide encapsulation chemistry, by virtue of its coordinative symmetry, which is lower than the normally noted O_h-symmetry (*e.g.*, in **4**).[6] As pointed out earlier, while a recurrent feature of the discussion of oxide-containing systems such as **5** is their description as a co-complex of the type $(LiR)_n\cdot Li_2O$, designation of the Li_2O fragment has often been arbitrary for symmetry reasons. In this context, the C_2-symmetric structure of **5** reveals a near linear [Li–O–Li = 175.8(2)°] lithium oxide moiety for which the mean Li–O distance of 1.803 Å compares with a mean of 1.869 Å for the remaining Li–O bonds. The result is that the Li_2O moiety can be viewed as being sandwiched between two twisted $Li_2(N_2C)_2$ ladders.[4] This symmetry is, however, not retained in benzene solution, where ^7Li NMR spectroscopy reveals two signals and thus points to a higher average symmetry (D_2) species.

While the monolithiated species discussed above have been suggested to perform oxygen scavenging in the presence of moisture, so too have dilithiates been noted to incorporate oxide ions in a cage-like environment. This was first noted by Gais *et al.* in 1988 when the geminal nature of dimetallation in the dilithiosulfone $\{Li_2[C(SiMe_3)SO_2Ph]\}_n$ was extrapolated based on the solid-state structure of $(THF)_{10}\cdot Li_{14}[C(SiMe_3)SO_2Ph]_6(O)$ **6**.[8] It is reported that the reaction of $H_2C(SiMe_3)SO_2Ph$ with two equivalents of Li^nBu in the presence of Li_2O, the source of which is not commented on by the authors, affords sparingly soluble prismatic crystals of **6**, whereas reaction in the absence of Li_2O yields readily soluble octahedral crystals which prove to be the chiral complex $(THF)_7\cdot[Li_2C(SiMe_3)SO_2Ph]_4$ **7**. More recently, the solid-state structures of heterochiral aggregates of the mixed α-mono- and α,*ortho*-dilithiated sulfoximine $(TMEDA)_3\cdot Li_8[C(H)(Me)S(=O)(Ph)=NMe]_2\cdot[C(H)(Me)S(=O)(C_6H_4)=NMe]_2(O)$ **8** (Fig. 3)[9] and of the α,α-dilithiated sulfoximine $(THF)_6\cdot Li_{10}[C(Ph)S(=O)(Ph)=NMe]_4(O)$ **9** (Fig. 5b)[10] have been reported. Reaction of *racemic* $H_2C(Me)S(=O)(Ph)=NMe$ with Li^nBu in TMEDA yields **8**, the solid-state structure of which reveals chiral resolution within each aggregate such that the two α-metallated sulfoximine monoanions adopt an (*S*)-configuration while the two α,*ortho*-metallated dianions are both (*R*)-isomers (Fig. 4). The oxide ion, assumed to arise from LiOH contamination of the commercial organolithium reagent, resides at the structure core and interacts with six of the eight alkali metal centres present. The monolithiated moiety reveals a motif new to singly charged sulfoximines inasmuch as the α-Li centre interacts with neither the oxygen nor the nitrogen centres in the same unit but resides *gauche* with respect to these atoms and is, instead, intermolecularly supported by TMEDA solvation and the O-centre of a dianionic sulfoximine moiety (Fig. 4a). These latter fragments reveal interactions between both metal centres and the deprotonated *ortho*-aromatic position with the two alkali metals being stabilised by intramolecular coordination from oxygen and nitrogen. The α-C lone pair adopts a *gauche* conformation with respect to nitrogen and to the deprotonated aromatic ring (Fig. 4b).[9] X-Ray crystallography reveals that the polymetallated product (**9**), obtained when $H_2C(Ph)S(=O)(Ph)=NMe$ is treated with 2.5 equivalents of Li^nBu in the presence of approximately one-third of an equivalent of H_2O (supplied as a stock solution in THF), is racemic, has two different types of dimetallated carbanionic centres in the asymmetric unit and incorporates a tetracationic hexalithium oxide core which acts as a nucleation site for the aggregation of four dilithiated sulfoximine dianions. This view of templated self-assembly has its origin in the observation that the solid-state structure of the monolithiated sulfoximine analogue $[TMEDA\cdot LiC(H)(Ph)S(=O)(Ph)=NMe]_2$ (Fig. 5)a is based on an eight-membered $(LiNSO)_2$ ring motif of a kind which is preserved in the periphery of **9** (Fig. 5b). In consequence, the best way to view the latter structure is as a co-complex in which an Li_6O^{4+} core is encapsulated by four monolithiated sulfoximine anions.

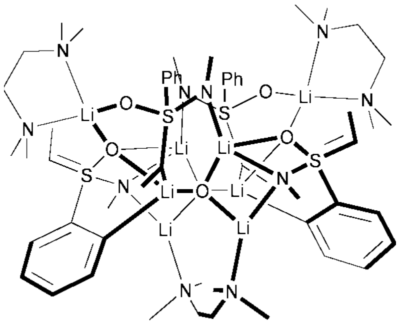


Fig. 3 Racemic $H_2C(Me)S(=O)(Ph)=NMe$ reacts with Li^nBu in TMEDA to give **8**.

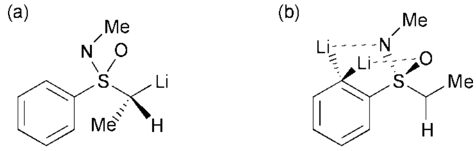


Fig. 4 Chiral resolution means that (a) the α-metallated monoanions in **8** have an (*S*)-configuration while (b) the α,*ortho*-metallated dianions are (*R*)-isomers.

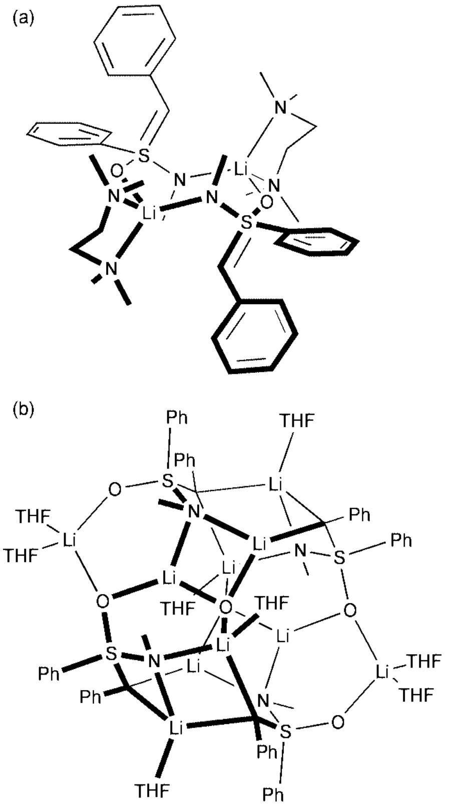


Fig. 5 (a) The structure of $[TMEDA\cdot LiC(H)(Ph)S(=O)(Ph)=NMe]_2$ suggests that (b) that of α,α-dilithiated $(THF)_6\cdot Li_2[Li_2C(Ph)S(=O)(Ph)=NMe]_4(O)$ **9** is templated by an Li_6O^{4+} core.

Oxide capture cage complexes have also been afforded by the synthesis of higher Group 15 salts in the presence of trace oxygen. In this context, investigations into the structures and reactivities exhibited by dilithium (silyl)phosphanediides and arsanediides have revealed that, empirically, R_3EH_2 [R = $^iPr_2(Mes)Si$ (Mes = mesityl), E = P; R = $Me_2(^iPrMe_2C)Si$, E = As (see below)] reacts with Li^nBu–Li_2O to afford octameric and dodecameric aggregates, respectively.[11] The former of these products, $Li_{18}(PR_3)_8(O)$ **10**, incorporates a pseudo-octahedral core that contains a μ_6-coordinated oxide ion. The structure is best viewed as a significantly distorted P_8 cube, each edge of which is bridged by one Li centre of a larger Li_{12} arrangement and each face of which is capped by one Li centre of the core Li_6O^{4+} motif. Efforts to establish whether the tetracationic hexalithium oxide core acts as a nucleating agent (see above) for the crystallisation of species such as **10** have led to the synthesis of $Li_6(PSi^iPr_3)_{10}$ in the strict absence of Li_2O.[12] Moreover, it has been noted that the reaction of $H_2PSi[C(^iPr)Me_2]_3Me_2$ (= H_2PR) with Li^nBu in the ratio 2 : 3 and in the presence of a small amount of LiOH in toluene affords the partially lithiated dodecameric species $Li_{20}(PR)_6(HPR)_6(O)$ **11** (Fig. 6a), which reveals an 'open' three-dimensional, cyclised

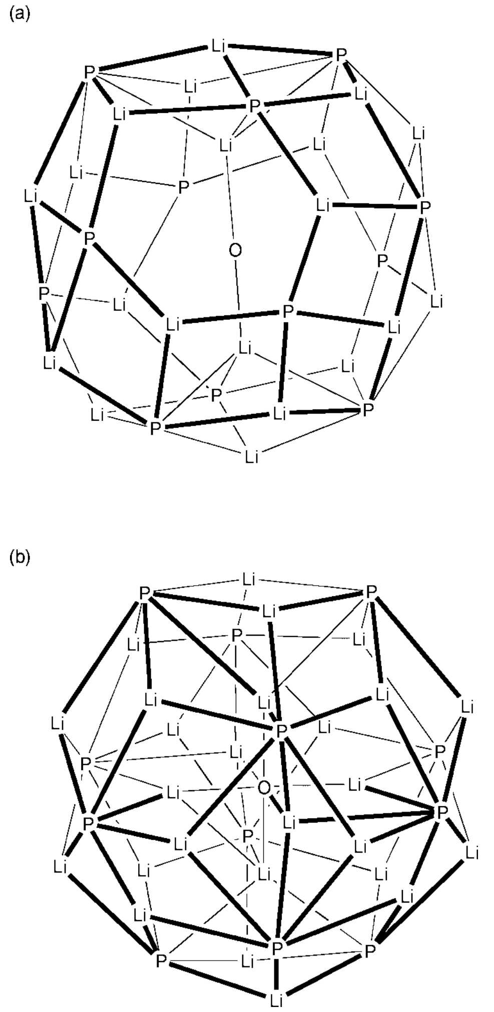


Fig. 6 (a) A structure-determining linear Li_2O fragment resides at the core of dodecameric $Li_{20}(PR)_6(HPR)_6(O)$ **11**, which (b) goes on to form closed-shell $Li_{26}(PR)_{12}(O)$ **12** {R = Si[C(^{i}Pr)Me$_2$]$_3$Me$_2$}.

$Li_{18}P_{12}$ ladder that encapsulates a structure-determining, linear lithium oxide moiety. The same study has determined that **11** is an intermediate in the formation of the fully-metallated closed-shell complex $Li_{26}(PR)_{12}(O)$ **12** (Fig. 6b) and that the icosohedral P_{12} architecture noted in **11** is maintained in this latter complex.[12] Both **11** and **12** largely retain their structural integrity in solution. Hence, ^{31}P NMR spectroscopy on **11** in [$^2H_8$]THF reveals two singlets (δ −365, −362) and one doublet (δ −301) for the PLi_2 and PHLi ($^1J_{PH}$ = 152 Hz) moieties, respectively, while ^{7}Li NMR spectroscopy affords three signals (δ 1.10, 1.40, 5.56) in a 1 : 2 : 4 ratio. Moreover, the ^{7}Li NMR spectrum of **12** reveals resonances (δ −1.70, −0.80, 2.10) in a 1 : 2 : 10 ratio.

One example of a higher denticity homometallic oxide encapsulation complex has been reported. A cuboidal array of Li centres surrounds a μ_8-O^{2-} ion in the complex $Li_8(R)_6(O)$ **13** in which R is a 4-azabenzimidazole derivative [eqn. (2), M = Li, n = 8].[13] While it was first assumed that this synthesis was allowed by the serendipitous entry of moisture into the reaction mixture, attempts to generate **13** by the deliberate addition of liquid water failed, presumably because **13** is itself hydrolytically unstable [eqn. (1), M = Li]. To test the postulate that the original synthesis depended on the presence of trace water, vapour diffusion was employed. A vessel containing an ethereal solution of LiR was connected to a second flask which contained $CuSO_4{\cdot}5H_2O$. This was observed to slowly turn from blue to white with the concomitant, near quantitative formation of **13**. Lastly, the structural integrity and S_6-symmetry of **13** is retained in solution, with ^{7}Li NMR spectroscopy revealing two resonances in a 1 : 3 ratio.

3 Heterometallic complexes

3.1 Metal organo- and inorganooxides

The sequential reaction of $ZnMe_2$ with various 2-pyridylamines [HN(2-C_5H_4N)R, R = Ph, 3,5-Xy (= 3,5-xylyl), 2,6-Xy], Li^{t}Bu and thereafter either with air (dried over P_2O_5) *or* molecular oxygen has afforded various lithium zincate species by complex pathways.[14] The amine HN(2-C_5H_4N)Ph has been found to give both the dimer of THF·Li(OMe)Zn[N(2-C_5H_4N)Ph]$_2$ **14** (Fig. 7a) and the trigonal bis(O^{t}Bu)-capped Li_2Zn complex, (THF·Li)$_2$[(μ_3-O)^{t}Bu]$_2$Zn[N(2-C_5H_4N)Ph]$_2$ **15** (Fig. 7b). In the solid state, **14** reveals a structure which is built around a planar $(ZnO)_2$ ring (mean Zn–O = 2.016 Å) in which each zinc centre is tetrahedral with oxygen having empirically inserted into the Zn–C bond of a {MeZn[N(2-C_5H_4N)Ph]$_2$}$^-$ ion. The Li centres lie exocyclic to this $(ZnO)_2$ ring and are *anti*-disposed about it, each one interacting with one core O-centre and with two pyridyl N-centres. Since each of these two aromatic systems forms part of ligands which are themselves bonded to different Zn centres, LiO-edge-fused pairs of MOM′NCN 6-membered rings form with NCN fragments spanning Li–O–Zn moieties.

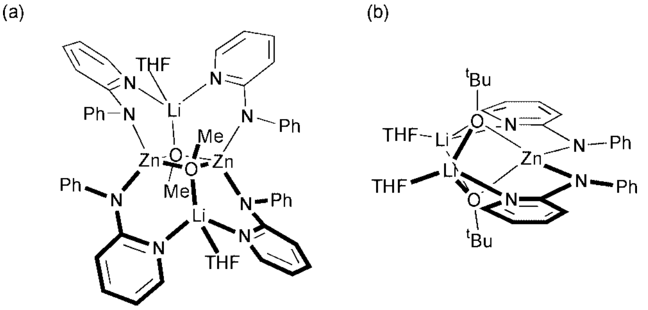


Fig. 7 Both (a) The dimer of THF·Li(Me)OZn[N(2-C_5H_4N)Ph]$_2$ **14** and (b) (THF·Li)$_2$[(μ_3-O)^{t}Bu]$_2$Zn[N(2-C_5H_4N)Ph]$_2$ **15** are isolated from the same mixed Zn–Li system.

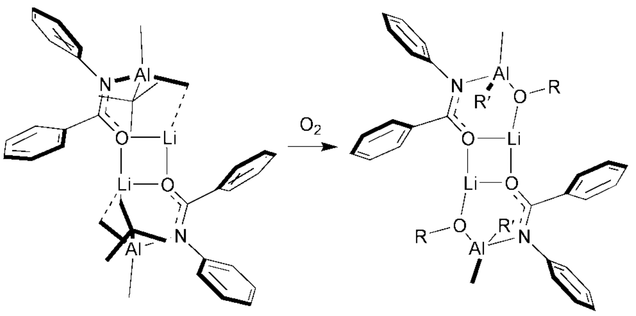
A complex reaction mechanism involving the formation of by-products is suggested by the observation that, in spite of the reaction stoichiometry, **14** incorporates two equivalents of pyridylamide ligand per zinc centre. This view is reinforced by the observation of a trace O^{t}Bu signal in the ^{1}H NMR spectrum of the product and it transpires that the synthesis of **14** is concomitant with that of **15**. In the solid-state this latter complex reveals a non-bonded triangular Li_2Zn core [Li···Li = 2.635(6) Å, mean Li···Zn = 2.607 Å], each heterobimetallic edge of which is spanned by a 2-pyridylamide ligand and the face of which is bis-capped by two *in situ* generated O^{t}Bu$^-$ ions. However, in spite of the known propensity for organolithium complexes to afford peroxide intermediates on exposure to oxygen,[1] the inter-oxygen distance [2.530(2) Å] in **15** does not suggest the presence of a peroxide moiety here. It appears that, empirically, the distortion of two fragments of LiO^{t}Bu electrostatically satisfies a zinc diamide. Thus, **15** is probably best described as a 2 : 1 LiO^{t}Bu–Zn[N(2-C_5H_4N)Ph]$_2$ adduct rather than as a dilithium tetraorganozincate.

Complex **16**, the precise structural analogue of **14**, results from the employment of HN(2-C_5H_4N)(3,5-Xy) in place of HN(2-C_5H_4N)Ph, while the use of more sterically congested HN(2-C_5H_4N)(2,6-Xy) has yielded a significantly different product, the composition and structure of which may be of importance in comprehending the mechanisms active in oxygenation processes inherent to systems of this type. X-Ray diffraction reveals this species to be dimeric [THF·Li(O^{t}Bu)-Zn(O^{t}Bu)Me]$_2$ **17**. Based on a $Li_2Zn_2O_4$ pseudo-cubic core, **17** is notable for the retention of labile Zn–C(Me) groups and the incorporation of asymmetric *tert*-butoxy capping of both Li_2Zn and $LiZn_2$ triangulated fragments akin to that noted in compounds **14–16**.

The formation of metal alkoxides has also been investigated in the context of mixed s-/p-block heterobimetallic complexes, with treatment of the amidoalane Me$_2$AlN(Me)C(O)Ph **18** with Li^{t}Bu affording the simple lithium aluminate {Li[^{t}Bu(Me)$_2$AlN(Me)C(O)Ph]}$_n$ **19**. Upon the introduction of air (dried over P$_2$O$_5$) this converts to the unusual mixed-anion complex {Li[^{t}Bu(Me)(MeO)AlN(Me)C(O)Ph]·Li[^{t}BuO(Me)(MeO)AlN(Me)C(O)Ph]}$_2$ **20**, as the only isolable product.[15] At its core this tetranuclear species has an (LiO)$_4$ ladder based on three (LiO)$_2$ rings which utilise the original carbonyl oxygen centres of the substrate. Peripheral to this arrangement are the two types of oxygenated aluminate anions which have been produced by aeration. These moieties act in distinct ways with two *mono*-oxygenated anions, [PhC(O)N(Me)Al(Me)(^{t}Bu)OMe]$^-$, using their *in situ* formed OMe groups to close 6-membered LiO(Me)AlNCO chelate rings at the ladder ends. In contrast, the two dioxygenated [PhC(O)N(Me)Al(Me)(O^{t}Bu)OMe]$^-$ ions act as tripodal ligands, spanning ladder end and central Li$^+$ ions using their O^{t}Bu and OMe units, respectively. The result is a series of edge-fused 6-membered rings. One, involving both types of Li centre, is based on an MO(M′O)$_2$ (M = Al, M′ = Li) heterocycle, while the other two each incorporate one alkali metal ion. To date, structurally characterised lithium aluminates have all incorporated intramolecular Li–O interactions based either on straightforward Al(μ_2-O)Li or Al(μ_2-O)$_2$Li motifs or else on LiO(AlO)$_2$ or (AlO)$_n$ rings (n = 2, 3). Just one example of a 4-membered (LiO)$_2$ ring core supported by peripheral Al(μ_2-O)$_2$Li heterocycles has been noted.[15]

Of note when considering the structure of **20** is the observation that the coordinative requirements of the two different types of Li centre present are satisfied by the variability with which ligand oxygenation occurs in **19**. Attempts to understand the processes active in the synthesis of **20** have led to the sequential lithiation and oxygenation (with P$_2$O$_5$ dried air) of Me$_2$AlN(Ph)C(O)Ph **21**, itself known to be a dimer based on an 8-membered (AlNCO)$_4$ heterocycle.[15] The first step of this reaction has afforded the lithium aluminate {Li[^{t}Bu(Me)$_2$AlN(Ph)C(O)Ph]}$_2$ **22** which is based on an essentially planar (LiO)$_2$ ring core that utilises the carbonyl O-centres of the precursor. Peripheral to this, the alkali metal centres are supported by intra- and inter-dimer agostic bonds involving certain of the Al-bonded alkyl groups. Subsequent oxygenation yields a dimer with an (LiO)$_2$ core similar to that in **22**. The aluminate anions have been *mono*-oxygenated and they utilise their *in situ* formed alkoxy groups to give the 6-membered LiO(R)AlNCO (R = ^{t}Bu or Me) rings which chelate the Li centres (*cf.* ladder interception by singly-oxygenated aluminate anions in **20**). In fact, ^{1}H NMR spectroscopy points to the oxygenated product being composed of a 70:30 **23a–23b** isomeric mixture whereby the complex empirically takes the form ½{Li[(RO)R′(Me)AlN(Ph)C(O)Ph]}$_2$ (R = ^{t}Bu, R′ = Me **23a**, R′ = ^{t}Bu, R = Me **23b**).[15] Though this ratio is borne out crystallographically by the best refinement of the Fourier difference map it is impossible to determine whether individual dimers comprise molecules with the same R and R′ groups in both halves. Moreover, *ab initio* methods lend weight to the view that oxo-insertion into an Al–C(^{t}Bu) bond represents the preferred reaction pathway by suggesting a 14.8 kcal mol^{-1} (62.0 kJ mol^{-1}) gain in stabilisation upon oxygenation of such a bond (and concomitant Li–O interaction) relative to that of an Al–C(Me) one in a Li[^{t}Bu(Me)$_2$AlN(H)C(O)H] monomer.

While **20** and **23** are reproducibly obtainable by exposing their respective lithium aluminate precursors to either untreated (that is, moist) or (P$_2$O$_5$) pre-dried air the former route affords products which are significantly contaminated. This points to the hydrolytic formation of alkylaluminoxanes[16]—a subject which has recently been the topic of review[17]—and suggests that molecular oxygen, rather than moisture, is active in the oxo-insertion processes reported for these aluminates. In both cases ligands are afforded which are ideal for the provision of additional coordination to the alkali metal centres, with the observed relationship between **22** and **23** suggesting that a template effect operates whereby exactly the right amount of oxygen is captured to remove all agostic stabilisation of the Li centres and to stabilise them using all of the generated alkoxy fragments, whilst retaining the (LiO)$_2$ core of the precursor (Scheme 1).

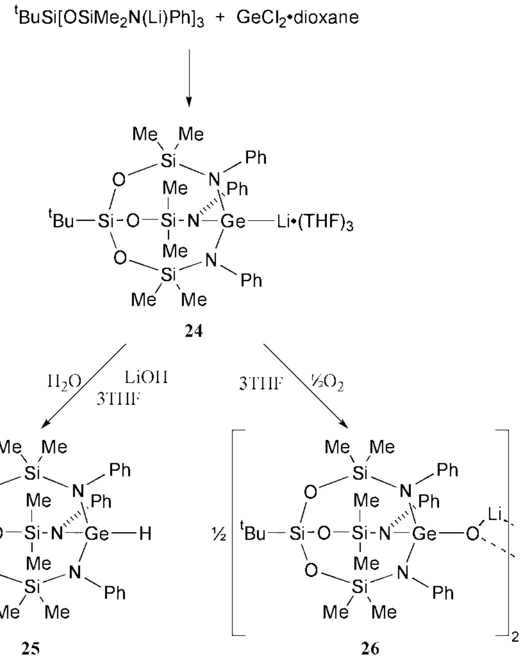


(**22**)$_2$ (**23**)$_2$

70: 30 **23a** (R = ^{t}Bu, R′ = Me): **23b** (R′ = ^{t}Bu, R = Me)

Scheme 1

Moving from Group 13 to Group 14, the reactivity towards both water and oxygen of the first germanium(II) siloxamide that incorporates a Ge–Li interaction has recently been probed (Scheme 2).[18] Reaction of the trilithium salt [LiN(Ph)SiMe$_2$O]$_3$Si^{t}Bu with GeCl$_2$·dioxane in THF affords (THF)$_3$·LiGe[N(Ph)SiMe$_2$O]$_3$Si^{t}Bu **24**. The controlled hydrolysis of this species yielded the corresponding hydride **25** by Li/H exchange, with the Group 14 metal centre formally adopting the +4 oxidation state (*cf.* mean Ge–N = 1.982 Å in **24**, mean Ge–N = 1.848 Å in **25**). However, the treatment of a benzene solution of **24** with molecular oxygen has incurred oxo-insertion into the metal–metal bond with the concomitant formation of a germanium(IV) centre (mean Ge–N = 1.860 Å) and an unsolvated lithium germanolate moiety **26**. This crystallises as a dimer based on an (LiO)$_2$ ring core (mean Li–O = 1.795 Å) with the alkali metal centres being rendered pseudo-tetrahedral



Scheme 2

by virtue of weak interactions with PhN groups. Perhaps the most remarkable feature about the structure of **26** is the shortness of the Ge–O bond [1.702(4) Å] relative both to the sum of van der Waals radii for germanium and oxygen and to other known germanium–oxygen bonds.[18]

3.2 Metal oxides

A new field has recently been developed by Mulvey whereby mixed Group 1–Group 2 metal amides are treated with compressed oxygen or air (dried over $CaCl_2$).[19] This initially led to the reproducible synthesis of a mixture of lithium tetramethylpiperidide (LTMP) and an oxide derivative of both the lithium and magnesium tetramethylpiperidide systems $Li_2Mg_2[N(CMe_2CH_2)_2CH_2]_4(O)$ **27**. Whereas preparation was originally by the treatment of an equimolar mixture of Li^nBu and Mg^nBu^sBu with oxygenated parent amine it has been noted that the use of two equivalents of the Group 2 metal reagent affords a substantially lower level of LTMP. An oxide anion resides at the centre of an eight-membered $Li_2Mg_2N_4$ metallocycle in **27** and this has led to the description of such systems as 'inverse crown ethers'.[20] Moreover, the $M_2M'_2O^{4+}$ core can be regarded, like the octahedral Li_6O^{4+} superstructures discussed above, as a simple, lipophilically wrapped inorganic lattice fragment. In the case of **27**, the similar sizes of Li^+ and Mg^{2+} have led to disorder preventing identification of the Group 1 and Group 2 metal centres. Attempts to circumvent this problem have led to the synthesis, isolation and structural characterisation of an analogue of this system which contains a higher Group 1 metal. Thus, a comparable motif to that noted for **27** has been reported for the mixed oxide–peroxide Na–Mg system $Na_2Mg_2(HMDS)_4(O_2)_x(O)_y$ [$x = 0.32$, $y = 0.68$] **28** (HMDS = 1,1,1,3,3,3-hexamethyldisilazane) with the oxide and peroxide complexes logically representing thermodynamic and kinetic products, respectively. More recent attempts to generate the K–Mg analogue have yielded infinite, agostically bonded chains of the uniquely peroxide trapping species $K_2Mg_2(HMDS)_4(O_2)$ **29**.[21] Attempts to generate the Li–Mg congener of this last HMDS complex have again afforded an oxide–peroxide mixture: $Li_2Mg_2(HMDS)_4(O_2)_x(O)_y$ [$x = 0.72$, $y = 0.28$] **30**—this time favouring the kinetic species. The most recent developments in this field have seen the syntheses of the first sodium–zinc and potassium–zinc inverse crown ethers, $Na_2Zn_2(HMDS)_4(O)$ **31** (Fig. 8a) and $K_2Zn_2(HMDS)_4(O_2)_x(O)_y$ [$x = 0.82$, $y = 0.18$] **32** (Fig. 8b), respectively. However, attempts to isolate the lithium–zinc analogues of **31** and **32** have, so far, proved unsuccessful with the polymeric adduct $[Li(\mu\text{-}HMDS)_2ZnMe]_\infty$ being obtained instead.[22] The employment of **30** *as a substrate* in conjunction with excess benzonitrile has revealed the μ_5-oxide $Li_4Mg[(NSiMe_3)_2C\text{-}Ph]_4(O)$ **33** in which the metal-oxide core is encapsulated by amidinate ligands which bond to the s-block ions with significant π-character and which are formed *in situ* by a well documented addition–migration process involving LiHMDS and PhCN.[23] Complex **33** reveals C_2 symmetry with the four Li^+ ions and the single Mg^{2+} ion describing an oxygen-centred, distorted trigonal bipyramid with the Group 2 metal centre residing in the equatorial plane [Li_{ax}–O = 1.799(11) Å, Li_{eq}–O = 1.919(11) Å, Mg–O = 1.850(6) Å].[23] Just one other mixed Li–Mg oxide-encapsulation cluster has been reported. Magnesium rich $(THF)_4{\cdot}LiMg_4[O(2\text{-}Me)C_6H_4)]_7(O)$ **34** has been isolated from a 2:1:4 mixture of Li^nBu, Mg^nBu_2 and 2-methylphenol in toluene–THF, yet, although the synthesis is reproducible, the oxygen source is not known.[24] Akin to **33**, the core of **34** adopts a distorted trigonal bipyramidal geometry with the Group 1 metal ion residing in the equatorial plane [Li–O = 1.89(2) Å]. That this ion bonds more strongly to the interstitial oxide ion than either the equatorial or axial magnesium centres [Mg_{ax}–O = 2.041(2) Å, Mg_{eq}–O = 2.002(4) Å] is probably a reflection of the relative coordination states of the different metals. Hence, whereas the Group 1 metal is only tricoordinate, each Group 2 metal is rendered pentacoordinate by virtue of μ_2-bridging of the Mg···Mg distances by the organic anion and by THF-solvation. A more complicated mixed s-block metal oxide-encapsulation complex has been afforded in the course of investigations into superbase structural chemistry by the 1:1:1 or 2:1:2 reaction of $LiN(H)^tBu$ with KO^tBu in the presence of TMEDA. The resultant hemisolvate, $(TMEDA)_2{\cdot}Li_8K_2(^tBuO)_8(O)$ **35**, is rendered unusual by virtue of its inclusion of a μ_8-oxo dianion.[13] Rather than being cubic, however, the array of eight Li^+ ions describe a distorted dodecahedron, each face of which is μ_3-capped by an O^tBu ligand. Moreover, two opposing sides of this polyhedron are bridged by TMEDA-solvated K^+ ions.[25]

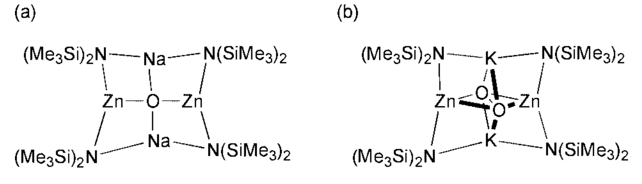


Fig. 8 The structures of (a) oxide and (b) peroxide capture metallocycles **31** and **32**, respectively.

A single example exists of a lithium-containing heterobimetallic oxide-encapsulation cluster in which the second metal type is a high Group 2 element. Hence, the sequential treatment of elemental barium with ^tBuOH and Li^nBu in THF–hexane has yielded an unusual heterobimetallic complex which X-ray crystallography reveals to be $Li_3(\mu_6\text{-}O)Ba_3(\mu_6\text{-}O)\text{-}[(THF)_3{\cdot}Ba_3](O^tBu)_{11}$ **36** (Fig. 9).[26] The interstitial oxide centres—the source of which remains ambiguous—reside in Ba_6 octahedral and Li_3Ba_3 trigonal prismatic environments. In the latter case, the oxide ion is displaced towards the Li_3-face of the heterobimetallic prism.

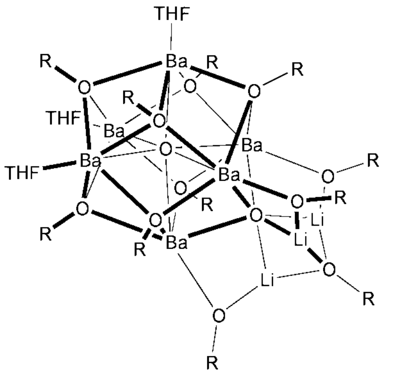


Fig. 9 The structure of $Li_3(\mu_6\text{-}O)Ba_3(\mu_6\text{-}O)[(THF)_3{\cdot}Ba_3](OR)_{11}$ (R = ^tBu) **36**.

Mixed s-/p-block heterobimetallic oxide-encapsulation clusters have also been noted. As has already been discussed, $[^iPr_2(Mes)Si]_3PH_2$ reacts with Li^nBu–Li_2O to afford octameric $Li_{18}(PR_3)_8(O)$ **10**.[11] In a similar vein, the arsenic analogue $[Me_2(^iPrMe_2C)Si]_3AsH_2$ reacts to form the topologically similar complex $Li_{26}(AsR_3)_{12}(O)$ **37**. It reveals a distorted As_{12} icosahedron, each face of which is capped by one of twenty Li centres to give an exterior of alkali metal ions (affording an I_h-symmetric $Li_{20}As_{12}{}^{4-}$ cluster). Internally, an Li_6O^{4+} array is orientated such that its C_3 axes coincide with those of the tetracationic outer-shell.[11] Moreover, research into the structure-defining properties of LiOH and Li_2O in the lithiation of primary silylphosphanes has been extended, with the same results, to primary silylarsanes.[12]

With a single exception, heterobimetallic oxide-encapsulating polyhedra incorporating higher alkali metals have been noted only for $M_2M'_4$ stoichiometry. Two examples of sodium-containing pseudo-octahedra have been reported to entrap oxide ions: whereas the 1 : 1 reaction of ½$[Bi(OC_6F_5)_3{\cdot}PhMe]_2$ with $NaOC_6F_5$ affords polymeric $THF{\cdot}Na(\mu\text{-}OC_6F_5)_2Bi(OC_6F_5)_2$, the employment of two equivalents of sodium reagent has been reported to yield both pseudo-octahedral $(THF)_4{\cdot}Na_4Bi_2(OC_6F_5)_8(O)$ **38** (by X-ray crystallography) and $(C_6F_5)_2O$ (by electron impact mass spectrometry).[27] The eight aryloxide ligands each cap a face of the octahedron but, as with the majority of other heterobimetallic pseudo-octahedra discussed here (see below), crystallographic disorder precluded unambiguous identification of the metal centres in the solid state. Instead, variable temperature ^{19}F NMR spectroscopy has been employed to reveal splitting of the aromatic centres. Ambient temperature spectroscopy shows just three aromatic signals—pointing to either *trans*-isomerism or rapid dynamic exchange. However, at 210 K each of these resonances is resolved into three lines with relative integrations of 1 : 2 : 1—suggesting *cis*-isomerism with two aryloxide groups capping Na_3 and $NaBi_2$ octahedron faces and with the remaining four ligands adopting Na_2Bi face capping modes. In a similar vein, *cis*-isomerism is suggested by the observation of three different types of edge-bridging trimethylsiloxide anion in the Sb(III) oxide–siloxide complex $Na_4Sb_2(OSiMe_3)_8(O)$ **39**, which, along with $(Me_3Si)_2O$, is formed by the reaction of $Sb(OSiMe_3)_3$ with two equivalents of $NaOSiMe_3$.[28] This evidence is provided by MAS NMR spectroscopy, with resonances in a 2 : 1 : 1 ratio being observed in both the ^{13}C and ^{29}Si NMR spectra.

A recent investigation into the formation of alkali(alkoxy) antimonates and bismuthates by Veith *et al.* has revealed that MO^tBu (M = Na, K) reacts with $E(O^tBu)_3$ (itself generated by the reaction of ECl_3 with 3^tBuOH in ammonia, E = Sb, Bi) in benzene to yield isobutene (characterised by ^1H NMR spectroscopy) and to then give $M_4E_2(O^tBu)_8(O)$ (M = Na, E = Sb **40**; M = Na, E = Bi **41**; M = K, E = Sb **42**, Fig. 10a) along with other products [eqn. (3)].[29] These results point to the elimination of isobutene from $ME(O^tBu)_4$ to give $ME(O^tBu)_3OH$ with the hydroxy group then acting as an oxide source in the formation of **40**–**42** [eqn. (4)]. The problem of crystallographic disordering of the metal centres noted above for **38** and **39** recurs in pseudo-octahedral **42**, but is solved rather ingeniously by its treatment with THF to give $(THF)_4{\cdot}K_4Sb_2(O^tBu)_8(O)$ **43** [eqn. (5) and Fig. 10b]. The solid-state structure of **43**, in which only the K centres are THF solvated, reveals an unusual, highly distorted octahedron, all eight faces of which are *tert*-butoxy capped. The shortest metal–oxide interactions are those involving the two antimony centres [2.004(5) Å] while those utilising the potassium ions *trans* to the Group 15 ions are relatively long [3.047(8) Å] as compared with the remaining $K–O^tBu$ bonds [2.624(10) Å]. Finally, the reactivity of $KSb(O^tBu)_4$ has been tested in the context of its sequential thermolysis and alcoholysis (with ^iPrOH). Remarkably the product, instead of being the alcoholate derivative of **43**, is an oxide–alkoxide, $K_4Sb_4(O\text{-}^iPr)_{12}(O)_2$ **44** (Fig. 10c), based on two O^{2-}-centred K_2Sb_2 tetrahedra [K–O = 2.693(4), Sb–O = 1.982(5) Å] with six face-capping isopropoxy groups. These distorted bimetallic tetrahedra are fused to one another *via* eight $K–O^iPr$ bonds (mean K–O = 2.836 Å).[29]

$$m\mathrm{ME(O^tBu)_4} \rightarrow n\mathrm{M_4E_2(O^tBu)_8(O)} + o\mathrm{Me_2C{=}CH_2} + p\,^t\mathrm{BuOH} + q\mathrm{E(O^tBu)_3} \qquad (3)$$

$$\begin{gathered}\mathrm{M = Na,\ E = Sb}\ \mathbf{40}\\ \mathrm{M = Na,\ E = Bi}\ \mathbf{41}\\ \mathrm{M = K,\ E = Sb}\ \mathbf{42}\end{gathered}$$

$$\mathrm{ME(O^tBu)_4} \rightarrow \mathrm{ME(O^tBu)_3OH} + \mathrm{Me_2C{=}CH_2} \qquad (4)$$

$$\underset{\mathbf{42}}{\mathrm{K_4Sb_2(O^tBu)_8(O)}} \xrightarrow{\mathrm{THF}} \underset{\mathbf{43}}{\mathrm{(THF)_4\bullet K_4Sb_2(O^tBu)_8(O)}} \qquad (5)$$

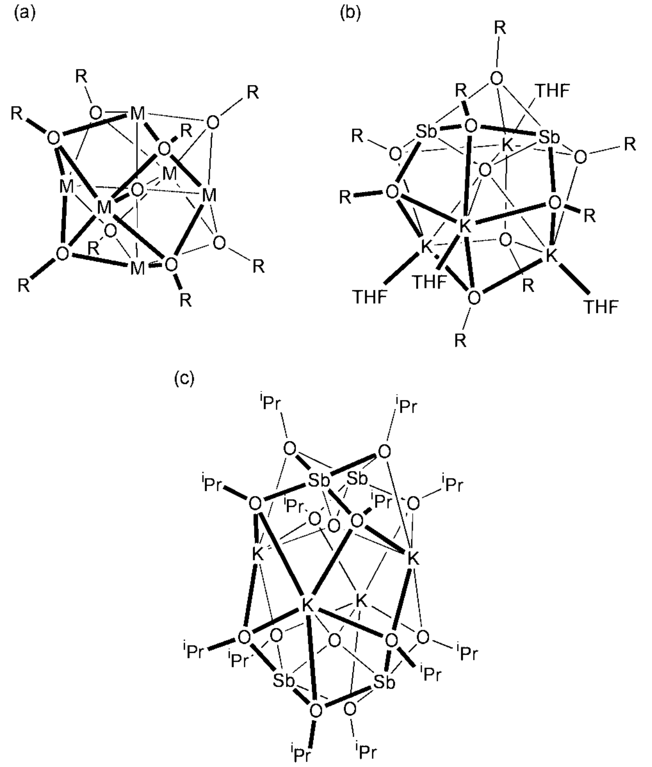


Fig. 10 Molecular structures of (a) $K_4Sb_2(OR)_8(O)$ **42** in which disorder prevents assignment of the metal centres (M = K, Sb; R = ^{t}Bu), (b) solvated $(THF)_4{\cdot}K_4Sb_2(OR)_8(O)$ (R = ^{t}Bu) **43**, and (c) the oxide–alkoxide alcoholate $K_4Sb_4(O^iPr)_{12}(O)_2$ **44**.

While few oxide capture octahedra have been reported to combine alkali metal with d-block metal chemistry one reported example of such a system is that of the adduct $[RuH(SiHPh_2)(CO)X_2]_2{\cdot}[Li_2Ru_4OCl_8X_4]$ (X = P^tBu_2Me) **45**. The complex is based on two square pyramidal $[RuH(SiHPh_2)(CO)(P^tBu_2Me)_2]_2$ units, both of which use their basal carbonyl ligands to act as 1,2-bridges to the alkali metal centres in the *trans*-$(\mu_6\text{-}O)Li_2Ru_4$ core, each face of which is μ_3-Cl capped. The oxide source is ascribed to hydroxide contamination of the Li^tBu used in the reaction.[30] The oxophilic nature of lithium is revealed in *two* ways by the structure of **45**: the interstitial oxide ion is bonded to each Li centre only marginally more strongly than the carbonyl O-centres that are utilised in adduct formation [Li–(μ_6-O) = 2.007(13), Li–OC = 2.033(14) Å].

It has been reported that the 1 : 2 reaction of $(THF)_4{\cdot}MnCl_2$ with lithium *N*,*N*′-dicyclohexylformamidinate in THF yields highly air-sensitive crystals which X-ray diffraction shows to be composed of the mixed-valence Mn(II)–Mn(III) oxide-encapsulation complex $LiMn_3[CyNC(H)NCy]_6(O)$ **46** (Cy = cyclohexyl).[31] The oxide ion resides at the centre of a heavily disordered tetrahedral array of metal centres while each of the six formamidinate ligands bridges an edge of the polyhedron. The organic residues do not lie coplanar with the two bridged metal centres but are skewed, causing the N-centres to adopt a slightly pyramidal geometry. It is claimed that the transition metal-induced deoxygenation of THF is responsible for the formation of **46**—this postulate being based on literature precedents for THF cleavage in the presence of oxophilic, strongly reducing transition metals.[31] However, the inability of this process to fully explain the observation of concomitant *n*-butane production (as the only detectable volatile) points strongly to the operation of a more complex mechanism in this system.

The work discussed above on templated oxygen scavenging reactions of lithium aluminates[15] has been extended to mixed Li–Zn systems[14] and has led to the isolation and structural characterisation of both the homometallic, oxide-capturing distorted tetrahedron $Zn_4[N(2\text{-}C_5H_4N)CH_2Ph]_6(O)$ **47** and the heterobimetallic oxide–alkoxide *fac*-$^tBuOLi_3Zn_3[(2\text{-}C_5H_4N)NMe]_6(O)$ **48** (Fig. 11). These complexes both empirically incorporate a $\{(\mu_3\text{-}O)Zn_3[N(2\text{-}C_5H_4N)R]_6\}^{2-}$ (R = CH_2Ph **47**, Me **48**) ligand which acts as a tetradentate donor to a Zn^{2+} ion in **47** and as a heptadentate donor to a $(Li_3O^tBu)^{2+}$ ion in **48** by virtue of flexibility in the orientations demonstrated by certain of the $[N(2\text{-}C_5H_4N)R]^-$ moieties. Thus, three Zn-centres in **47** describe the base of a trigonal pyramid, each edge of which is spanned by a $[N(2\text{-}C_5H_4N)CH_2Ph]^-$ ligand. The final zinc centre occupies the C_{3v} cluster apex and is stabilised by the pyridyl N-centres of the remaining three organic residues, each of which spans one non-bonding base–apex pyramid edge. At the core of C_{3v} cluster **47** is a nearly tetrahedral O^{2-} centre (mean Zn–O = 1.903 Å, mean Zn–O–Zn = 108.9°). However, the Li_3 face in **48** is μ_3-capped by an O^tBu group, suggesting the insertion of an oxygen atom into an Li–C(^tBu) bond [Li–O = 1.849(14) Å, Li–O2–Li = 83.7(7)°]. The three lithium centres bond less strongly to the encapsulated oxide ion in **48** [Li–O = 2.074(13) Å, Li–O1–Li = 73.0(6)°], which in turn interacts with the three Zn centres [Zn–O1 = 1.944(4) Å, Zn–O1–Zn = 101.4(3)°] to afford a molecular *fac*-isomeric $(\mu_6\text{-}O)M_3M'_3$ distorted octahedron. The coordination spheres of both the Li and Zn centres are completed by $[N(2\text{-}C_5H_4N)Me]^-$ ligands. Of these, three span the Zn···Zn distances in the lower tier of the cluster (as shown in Fig. 11) while three circumscribe the Li_3 upper tier but are orientated such that their NMe-groups span non-bonding Li···Zn octahedron edges.[14,32]

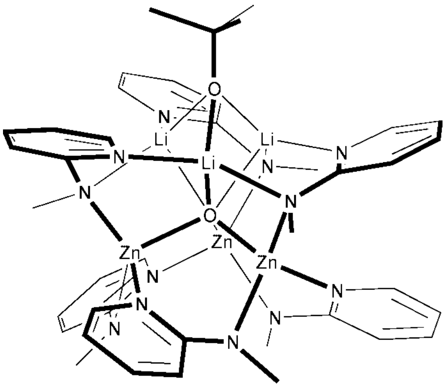


Fig. 11 Heterobimetallic *fac*-$^tBuOLi_3Zn_3[(2\text{-}C_5H_4N)NMe]_6(O)$ **48** reveals a $\{(\mu_3\text{-}O)Zn_3[N(2\text{-}C_5H_4N)Me]_6\}^{2-}$ heptadentate ligand which chelates a $(Li_3O^tBu)^{2+}$ ion.

Analogous complexes containing potassium and a d-block metal have also been reported. Hence, it has been noted that $Zr_2(O^iPr)_8(^iPrOH)_2$ reacts with an equimolar amount of potassium hydride in THF or pentane to yield $KZr_2(O^iPr)_9$ **49** which NMR spectroscopy suggests has C_{2v}-symmetry. Moreover, in the presence of DME the trigonal heterobimetallic complex DME·$KZr_2(O^iPr)_9$ DME·**49** (Fig. 12a) is afforded [eqn. (6)] with spectroscopic methods suggesting that the structure of this ether complex is analogous to that of unsolvated **49**. The presence of a second equivalent of KH has been found to afford both **49** and the *trans*-isomer of $K_4Zr_2(O^iPr)_{10}(O)$ **50** [eqn. (7) and Fig. 12b] [mean K–(μ_6-O) = 2.797 Å, mean Zr–(μ_6-O) = 2.044 Å].[33] The possibility that contamination of the metal hydride (with KOH) accounts for the oxide source is eliminated by the employment of KHMDS in place of KH. Moreover, effecting the transformation in silylated glassware and vacuum transferring the volatiles to an NMR tube has allowed the observation (by ^1H NMR spectroscopy) of propane, isopropyl alcohol and acetone as by-products of complex formation. Lastly, since the treatment of **49** with three equivalents of KO^iPr also affords **50**, it is deemed most likely that heterolysis of an O–$CHMe_2$ bond in $KZr_2(O^iPr)_9$ accounts for the presence of encapsulated oxide in **50**, with propane resulting and acetone formation providing the hydrogen necessary for its formation. More recently, as part of a study into the syntheses of zirconium aryloxides that bear pendant vinyl chains, the zirconium alkoxide '$Zn(OEt)_4$' has been treated with KOAr [OAr = $(2\text{-}MeO)\text{-}(4\text{-}CH_2{=\!=}CHCH_2)\text{-}OC_6H_3$] to give $K_4Zr_2(OEt)_2(OAr)_8(O)$ **51**, which, like **50**, crystallises as a *trans*-isomer [mean K–(μ_6-O) = 2.947 Å, Zr–(μ_6-O) = 2.0169(8) Å] in which each octahedral zirconium centre bears an ethoxide ion and the aryloxy ligands each cap a face of the K_4Zr_2O octahedron with alkali metal ions being eight coordinate.[34]

$$Zr(O^iPr)_8(^iPrOH)_2 + KH \xrightarrow[\text{DME}]{C_5H_{12}} \text{DME}{\cdot}KZr_2(O^iPr)_9 + {}^iPrOH + H_2$$

$$\text{DME} \bullet \mathbf{49} \qquad (6)$$

$$Zr_2(O^iPr)_8(^iPrOH)_2 + 2KH \ ^{\text{THF}} \quad KZr_2(O^iPr)_9 + K_4Zr_2(O^iPr)_{10}(O)$$

$$\mathbf{49} \qquad\qquad \mathbf{50} \qquad (7)$$

Lastly, the reaction of CsCl with $In(CH_2Ph)_3$ in acetonitrile has recently been reported to afford the trichloroindate complex $Cs(\mu\text{-}Cl)In(CH_2Ph)_3$, the recrystallisation of which from toluene–Et_2O affords a dimeric species based on a $(CsCl)_2$ ring with the Group 1 metal ions each being both intra- and intermolecularly η^6-stabilised by the aromatic components of several indium-bonded benzyl groups.[35] While the reaction of $In(CH_2Ph)_3$ in toluene with dry O_2 has been found to yield what cryoscopic relative molecular mass determination in benzene and infra-red spectroscopy suggest to be $[(PhCH_2)_2In\text{-}OCH_2Ph]_2$ **52**, the comparable treatment of $Cs(\mu\text{-}Cl)In(CH_2Ph)_3$ in Et_2O has resulted in the isolation and solid-state characterisation of the remarkable oxide–organooxide product $Cs_2In_4(CH_2Ph)_4(OCH_2Ph)_8(O)$ **53** (Fig. 13). This species can be regarded as being composed of an In_4O_8 metalla(crown ether) ring through which a linear Cs_2O [Cs–O = 3.4191(6) Å] molecule is threaded to give an $M_4M'_2O_8$ oxide-trapping cage.[29] Hence, the encapsulating $[PhCH_2In\text{-}(OCH_2Ph)_2]_4$ motif [based, as it is on four non-planar $(InO)_2$ rings which share In centres] mimics the action of 12-crown-4 in coordinating to the two alkali metal centres. Lastly, these metal ions are each supported by η^6-interactions to four benzylic π-systems.[35]

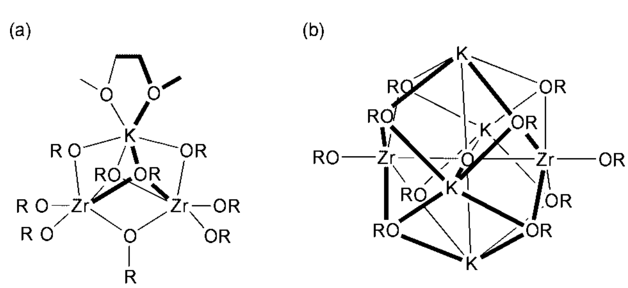


Fig. 12 (a) DME·$KZr_2(OR)_9$ DME·**49** is thought to be structurally analogous to an intermediate in the formation of (b) *trans*-$K_4Zr_2(OR)_{10}(O)$ **50** (R = ^iPr).

4 Concluding remarks

As discussed here, the reactivity of Group 1 organometallic compounds and Group 1-containing polymetallic compounds towards oxygen, in conjunction with the increased accessibility of X-ray crystallography has led to the structural characterisation of a variety of oxygenated compounds. However, few papers in the field have confidently identified the oxygen source and even fewer propose detailed mechanisms for the oxygen

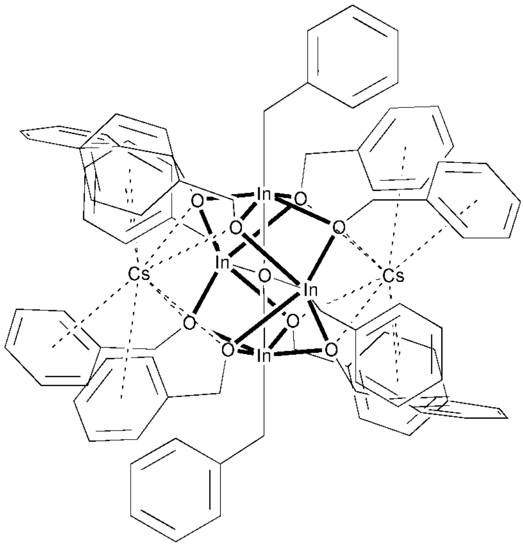


Fig. 13 Oxide-encapsulation cluster $Cs_2In_4(CH_2Ph)_4(OCH_2Ph)_8(O)$ **53** is best viewed as comprising a In_4O_8 metalla(crown ether) through which a Cs_2O molecule is threaded.

scavenging reactions. It is clear, however, that two basic structure types result from the oxygen scavenging properties of alkali metal-containing metallo-organic complexes. The encapsulation of an interstitial oxide has been revealed in both a homo- and heterobimetallic context, with the overwhelming preference in each case being for octahedral coordination of the chalcogenide centre. While examples of μ_8-oxides have been noted,[13,25] the most significant variants in this context are the tetrahedral oxide complex $K_4Sb_4(O^iPr)_{12}(O)_2$ **44**[29] and square planar 'inverse crown ethers'.[19–22] The latter of these systems are also notable by virtue of their ability to reveal rare peroxide-capture motifs. Caesium indate $Cs_2In_4(CH_2Ph)_4(OCH_2\ Ph)_8(O)$ **53** reveals oxide encapsulation in tandem with the second main mode of oxygen incorporation;[35] metal organo-and inorgano-oxide formation. This latter oxygen capture method has been noted in both organolithium and polymetallic systems and has afforded insights into the nature and mechanism of metal–carbon bond activation. Interestingly, the structures of certain lithium 'ate complexes have highlighted the role of the alkali metal component in oxygen capture.[15] Finally, whereas serendipitous oxygen capture has been reported, it is clear that the deliberate and controlled exposure of reactive organometallic complexes to oxygen can yield much useful information about the nature of their oxophilicity.

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