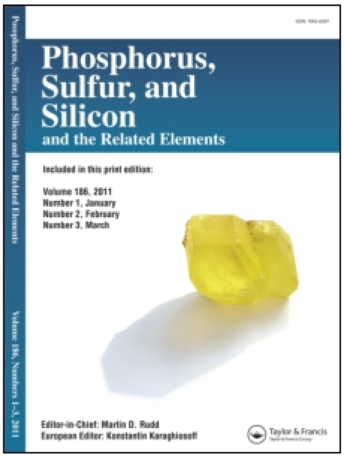

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Ligand Effects in the Syntheses of Molecular Main Group Metal Species Containing Interstitial Hydride

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In seeking to investigate whether structures of the type observed for $\{[\mathrm{Me_3Al(TMP)}]\mathrm{Li}\}_\infty$ (TMP = 2,2,6,6-tetramethylpiperidide) can be oligomerised by the use of polyfunctional N-centred ligands, we report lithium aluminates incorporating $\mathrm{RN\overset{\cdots}{-}C(H)\overset{\cdots}{-}NR}$ residues. For $\mathrm{PhN\overset{\cdots}{-}C(Ph)\overset{\cdots}{-}NPh}$ = Am cluster cation-containing $(\mathrm{Li_4Am_3})^+\cdot\{\mathrm{Li}[(\mu\text{-Me})_2\mathrm{Al(Me)Bu^t}]_2\}^-$ is afforded. However, the empolyment of PhN(H)(2-pyr) (pyr = pyridyl) instead affords both $\{\mathrm{Li_8(H)[N(2\text{-}pyr)Ph]_6}\}^+\cdot[\mathrm{Li(Me_2AlBu^t_2)_2}]^-$ and $\mathrm{Li_7(H)[N(2\text{-}pyr)Ph]_6}$: the first molecular Main Group clusters to incorporate interstitial hydride. Results indicate that β-elimination from $\mathrm{Bu^tLi}$ represents the source of $\mathrm{H^-}$ in these reactions.

Keywords: aluminium; 'ate complex; interstitial hydride; lithium; solid-state structure

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INTRODUCTION

The ability of lithium-containing heterobimetallic species to effect organic transformations[1] with different selectivity to those afforded by homometallic organolithium reagents has led to increased interest in their structural properties. For example, whereas organolithium reagents exhibit 1,2-addition towards α,β-unsaturated ketones,[2] conjugate addition has been reported in the presence of sterically congested organoaluminium compounds.[3] Lately, studies in which *bis*(aryloxy)methylalanes [$MeAl(OAr)_2$ (Ar = aryl)] have been reacted with organolithium species have afforded lithium aluminate monomers, $Me_2Al(\mu_2\text{-}OAr)_2Li$, of a type which are implicated in the 1,4-addition process.[4] Recently, attempts to extend such structural studies to N-centred ligands have led to the isolation and characterisation of [Me_3Al(TMP)]Li (TMP = 2,2,6,6-tetramethylpiperidide) **1**.[5] X-ray crystallography reveals infinite linear chains afforded by the intermolecular stabilisation of the lithium centres, otherwise only intramolecularly coordinated by the piperidide

N-centre in $Al(\mu_2\text{-}N)Li$ mode—by one of the three Al-bonded methyl groups.[6] We report here on attempts to study oligomerised analogues of this species by the utilisation of polyfunctional N-centered ligands and the isolation and structural charcterisation of the first Main Group clusters that encapsulate a hydride anion.

RESULTS AND DISCUSSION

The use of symmetrical formamidine ligands [R(H)N–C(H)=NR; R = 3,5-xylyl **2**, Ph **3**][7] yields simple lithium 'ate complexes $\{Me_2Bu^tAl[N(R)\overset{\cdots}{-}]_2CH\}Li$ (R = 3,5-xylyl **4**; Ph **5**). In the solid state these species show analogous monomers with, in each case, Li and Al centres bonding uniquely to a different nitrogen atom, the dispositions of the two metals being *trans* about the $[N(R)\overset{\cdots}{-}]_2CH$ unit in both cases.

Use of the more sterically demanding ligand N,N-diphenylbenzamidine (AmH) results in the isolation and structural characterization of a polymer based on fused tetranuclear Li_4-cluster cations and lithium *bis*(aluminate) anions; $(Li_4Am_3)^+\cdot\{Li[(\mu\text{-}Me)_2Al(Me)Bu^t]_2\}^-$ **6**.[8] While the cationic fragments are based on a charged Li-N cluster, the anions contain two Al centres arranged such that two of the methyl substituents on each are disposed tetrahedrally about Li, affording a $LiAlEt_4$-like $Li[(\mu\text{-}C)_2Al]_2$ motif.[9]

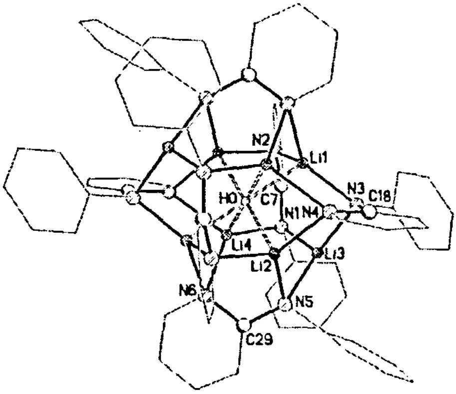

FIGURE 1, Molecular structure of the $\{Li_8(H)[N(2\text{-}Pyr)Ph]_6\}^+$ component of **8**

An anion of the type discussed above is also observed in the solid-state structure of one of the products of reaction between $Me_2AlN(2\text{-}Pyr)Ph$, **7**, and Bu^tLi in toluene. X-ray crystallography reveals the remarkable ion-separated compound $[Li(Me_2AlBu^t_2)_2]^- \cdot \{Li_8(H)[N(2\text{-}Pyr)Ph]_6\}^+$ **8**, which is the first example of a Main Group metal cluster to encapsulate a hydride anion.[10] The cationic part of **8** (FIGURE 1) is based on a $(Li^+)_8$ cubic cage whose six faces are straddled by the N–C=N backbones of the organic moieties (mean Li–N = 2.047 Å). While six Li^+ ions each interact with one deprotonated and two neutral N-centres, two (Li3 and Li3A) bond to just three deprotonated N-centres and are concomitantly extruded.

The central hydride in the cation is consistent both with the $[Li(Me_2AlBu^t_2)_2]^- : \{Li_8[N(2\text{-}Pyr)Ph]_6\}^{2+}$ stoichiometry and with the observed Li-H distances. The previously noted displacement of two Li centres facilitates the adoption of an octahedral coordination sphere by H^- [mean Li–H0 = 2.015 Å, *cf.* $(LiH)_\infty$[11] wherein Li–H = 2.04 Å] with neither extruded Li^+ ion bonding to H^- [Li3···H0 = 2.828(9) Å]. Preliminary *ab initio* M. O. calculations (6-31G* basis set at S.C.F. level) on cube-based $\{Li_8[N(H)CH_2NH_2]_6\}^{2+}$ predict a stable species if H^- is inserted into its Li_8 cavity, lending support to the observation of the cationic part of **8**. Moreover, the distortion noted for the cation of **8** are reproduced by this optimised structure, with two Li^+ ions extruding (Li···H = 3.45 Å) and the remainder rendering H^- octahedral (Li–H = 2.11 Å).

The temperature dependency of interstitial hydride formation is revealed by treatment of the reaction mixture with THF. While **7** is still afforded at room temperature, at +5 °C a mixture of $(Li{\cdot}4THF)^+{\cdot}[Li(Me_2AlBu^t_2)_2]^-$ **9**, and a species which X-ray crystallography reveals to be the second hydride-containing cluster $Li_7(H)[N(2\text{-}Pyr)Ph]_6$ **10** deposit. The structure of **10** is similar to that of the cationic part of **8** but has one Li^+ ion missing. The Li-centre *trans* to the vacant site shows an extended Li···H distance [2.49(3) Å] and renders H^- pseudo-seven-coordinate with this metal centre capping one face of a distorted octahedral coordination shell. The remaining Li–H interactions in which are comparable to those in **8** [mean Li–H = 2.06 Å].

Finally, the syntheses of **8** and **10** appear to critically depend on the choice of organolithium reagent. While treatment of **1** with Bu^nLi or Bu^sLi (as opposed to Bu^tLi) in THF affords **10** and analogues of **9**, it reacts with MeLi or $(Me_3Si)_2NLi$ to afford only the lithium 'ates $Me_3Al[N(2\text{-}Pyr)Ph]Li\cdot THF$ and $Me_2Al[(Me_3Si)_2N][N(2\text{-}Pyr)Ph]Li$ respectively. Thus it seems that β-elimination of LiH from the organolithium reagent is a criterion for the formation of **8** and **10**.[12]

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