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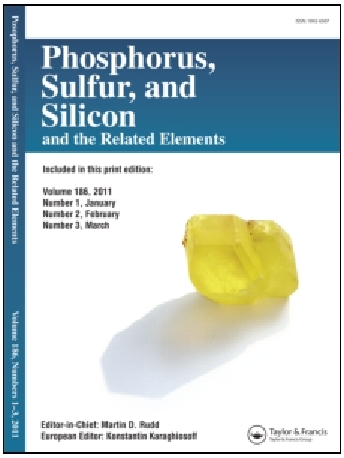

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Rings and Clusters Containing Polyimido and Imido/Oxo Anions of Group 13–15 Elements

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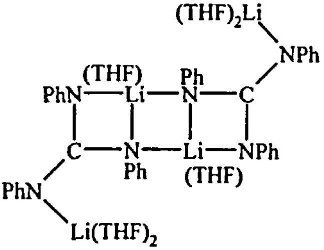
The dilithio boraamidinates $\{Li_2[RB(N^tBu)_2]\}_x$ (R = Me, ^nBu) are obtained by the reaction of $B[N(H)^tBu]_3$ with 3 equivalents of LiR. The X-ray structures of the dimer (R = ^nBu) and trimer (R = Me) consist of distorted Li_4N_4 cubes or Li_6N_6 hexagonal prisms capped by two or three BR groups, respectively. The lithiation of the dimers $\{M[N(H)^tBu]_3\}_2$ (M = Al, Ga) with LiR (R = ^tBu, Me) gives rise to complexes of the type $\{Li[Al(N^tBu)(NH^tBu)_2]\}_2{\cdot}(LiR)$ [R = ^tBu, $N(H)^tBu$] in which monomeric Li^tBu or $LiN(H)^tBu$ units are trapped by the dilithiated M_2N_6 template. The centrosymmetric dimer $\{THF{\cdot}Li_3[Si(N^iPr)_3(NH^iPr)]\}_2$, formed by trilithiation of $Si[N(H)^iPr]_4$ with Li^nBu, forms a bicapped hexagonal prism. The tetraazasilicate $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ is prepared by the reaction of $SiCl_4$ with 4 equiv. of $Li_2(Nnaph)$. Treatment of $OP[N(H)^tBu]_3$ with an excess of Li^nBu yields the dilithiated derivative $\{(THF)Li_2[OP(N^tBu)_2(NH^tBu)]\}_2$ with a box-shaped structure.

Keywords: Polyimido anions; Group 13–15 elements; lithium; rings; clusters

INTRODUCTION

The imido (NR) and oxo (O) ligands are isoelectronic. This overview will describe the synthesis and structures of imido analogues of the common oxo-anions CO_3^{2-}, BO_3^{3-}, AlO_3^{3-}, SiO_4^{4-} and PO_4^{3-}. Homoleptic polyimido and heteroleptic imido/oxo anions of the p-block elements are potentially versatile multidentate ligands. The lithium derivatives of these anions form aggregated polycyclic (cluster) structures.

The trisimidocarbonate dianions $[C(NR)_3]^{2-}$ (R = Ph,[1] ${}^tBu$[2]) have been prepared by two different routes. Bailey and co-workers described the synthesis of $\{Li_2[C(NPh)_3](THF)_3\}_2$ (**1**) by the dilithiation of *N,N′,N″*-triphenylguanidine with Li^nBu.[1] The THF-solvated complex **1** has an open ladder structure. In an alternative approach we generated $\{Li_2[C(N^tBu)_3]\}_2$ (**2**) by the reaction of the carbodiimide ${}^tBuN{=}C{=}N^tBu$ with $LiNH^tBu$ and, subsequently, Li^nBu.[2] The unsolvated complex **2** has a distorted cyclic ladder structure. Both **1** and **2** contain trigonal planar $[C(NR)_3]^{2-}$ dianions.



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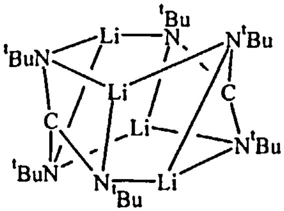

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BORAAMIDINATES

The hypothetical trisimidoborate trianion $[B(NR)_3]^{3-}$ is isoelectronic with $[C(NR)_3]^{2-}$. Our attempts to prepare this anion by the trilithiation of the trisamidoborane $B[N(H)^tBu]_3$ with organolithium reagents LiR (R = ^{n}Bu, Me) unexpectedly produced the boraamidinates **3**, **4a** and **4b** [Eq. (1)].[3]

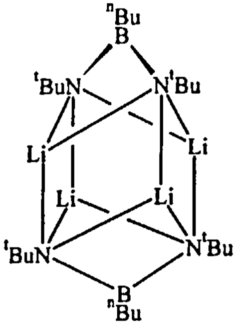
$$3LiR + B[N(H)^tBu]_3 \longrightarrow {}^1/_x\ \{Li_2[RB(N^tBu)_2]\}_x + LiN(H)^tBu + 2RH \quad (1)$$

3 (R = ^{n}Bu, x = 2)
4a (R = Me, x = 2)
4b (R = Me, x = 3)

The aryl boraamidinate $\{Li_2[PhB(N^tBu)_2]\}_n$ has been prepared by dilithiation of $PhB[N(H)^tBu]_2$.[4] This reagent was not structurally characterized, but it has been used in metathetical reactions to generate several main group derivatives, e.g. $[PhB(\mu\text{-}N^tBu)_2]_2Te$[5] and $[PhB(\mu\text{-}N^tBu)_2Pb]_2$,[6] and the transition-metal complex $[PhB(\mu\text{-}N^tBu)_2]_2Ti$.[4] The $[PhB(N^tBu)_2]^{2-}$ dianion acts as an *N,N'*-chelating ligand in all of these complexes.

X-ray structure analysis of **3** revealed a 10-atom ($Li_4B_2N_4$) cluster core isostructural with the $Li_4Si_2N_4$ framework in $\{Li_2[Me_2Si(N^tBu)_2]\}_2$.[7] The replacement of the ^{n}Bu group attached to boron by Me results in the formation of a less soluble product **4b**, in addition to the dimer **4a**. An X-ray structural determination of **4b** disclosed a novel trimeric arrangement based on a distorted hexagonal prism, for which alternate Li_2N_2 rings are *N,N'*-capped by a BMe unit.

The geometry at the three-coordinate boron atoms in **3** and **4b** is planar.



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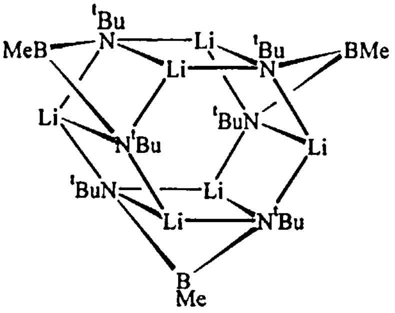
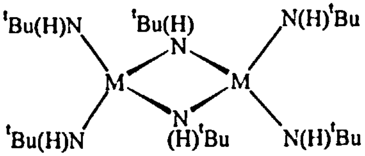


4b

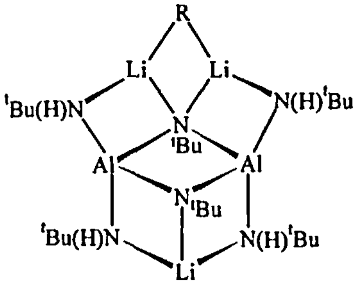
The formation of **3**, **4a** and **4b** involves cleavage of a B-N bond in favour of a B-C bond. In effect the reagent Li^{n}Bu functions both as a base to deprotonate two N(H)^{t}Bu groups of the B[N(H)^{t}Bu]$_3$ molecule and as a nucleophile to displace the third N(H)^{t}Bu group as LiN(H)^{t}Bu. Unlike the lithiation of bisamidoboranes RB[N(H)R']$_2$,[4] this new route to boraamidinates does not require the preparation of RBCl$_2$ reagents.

LITHIATION OF {M[N(H)^{t}Bu]$_3$}$_2$ (M = Al, Ga)

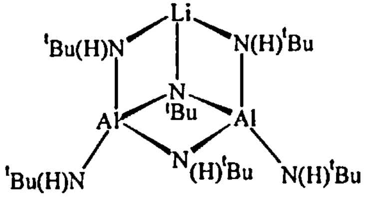


5a (M = Al); **5b** (M = Ga)

The dimeric trisamidoalane $\{Al[N(H)^tBu]_3\}_2$ (**5a**) is obtained as a 1:2 mixture of *cis* and *trans* isomers from the reaction of aluminum trichloride with six equivalents of $LiN(H)^tBu$.[8] The lithiation of this mixture by an excess of Li^tBu in *n*-hexane produced the complex $\{Li[Al(N^tBu)(NH^tBu)_2]\}_2{\cdot}(RLi)$ (**6a**, R = ^tBu) in which a monomeric Li^tBu unit is trapped by a dilithiated derivative of **5a**.[9] A structurally analogous complex $\{Li[Al(N^tBu)(NH^tBu)_2]\}_2{\cdot}(RLi)$ [**6b**, R = $^tBuN(H)$] is obtained when **5a** is treated with six equivalents of LiMe in diethyl ether. Thus it appears that LiMe acts both as a lithiating agent to produce the dilithiated derivative $\{Li[Al(N^tBu)(NH^tBu)_2]\}_2$ (**8**) and as a nucleophile to produce a monomeric $LiN(H)^tBu$ unit, which is trapped by **8**. NMR evidence indicates that lithiation of **5a** occurs preferentially at the $N(H)^tBu$ groups to give the monolithiated dimer **7** followed by **8**. Interestingly, the gallium analogue of **6b** is obtained in 47% yield from the reaction of **5b** with three equivalents of Li^tBu.[9]



6a $(R = {}^tBu)$
6b $[R = N(H)^tBu]$



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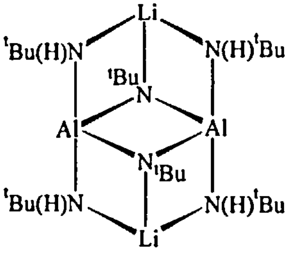

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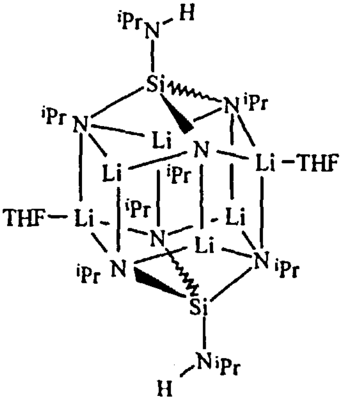
The trapping of Li^{t}Bu and LiN(H)^{t}Bu monomers by the dilithiated Al_2N_6 template is in distinct contrast to the behaviour of Li^{n}Bu. The reaction of **5a** with excess Li^{n}Bu produces the complex $Li_3\{Al_2(N^tBu)_3[N(H)^tBu]_3\}\cdot(Li^nBu)_2$ in which an *n*-butyllithium dimer is trapped by a trilithiated derivative of **5a**.[8]

THE $[Si(NR)_4]^{4-}$ TETRAANION

The tetrakisimido anions $[S(N^tBu)_4]^{2-}$ and $[P(Nnaph)_4]^{3-}$ have been structurally characterized as highly solvated, spirocyclic monomers $[Li(THF)_4^+]_x[(THF)_2\cdot Li(\mu\text{-}NR)_2E(\mu\text{-}NR)_2Li\cdot(THF)_2]^{x-}$ (E = S, x = O, R = ^{t}Bu; and E = P, x = 1, R = naph).[10,11] Attempts to generate the isoelectronic $[Si(NR)_4]^{4-}$ tetraanion by lithiation of $Si[N(H)^iPr]_4$ with an excess of Li^{n}Bu produced the dimeric trilithiated derivative $\{(THF)Li_3[Si(N^iPr)_3(NH^iPr)]\}_2$ (**9**) with a bicapped hexagonal prismatic structure. The tetraanion $[Si(Nnaph)_4]^{4-}$ can, however, be generated by treatment of $SiCl_4$ with $Li_2(Nnaph)$ in diethyl ether.[12]

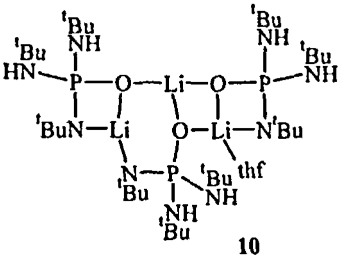
The product $(Et_2O{\cdot}Li)_4[Si(Nnaph)_4]$ was characterized by the formation of tetraprotonated and tetramethylated derivatives.[12]



9

LITHIATION OF $OP[N(H)^tBu]_3$

The lithiation of $OP[N(H)^tBu]_3$ with Li^nBu yields the trimeric monolithiated derivative $\{Li[OP(N^tBu)(NH^tBu)_2]\}_3{\cdot}thf$ (**10**) and the dimeric dilithiated derivative $\{(thf)Li_2[OP(N^tBu)_2(NH^tBu)]\}_2$ (**11**).



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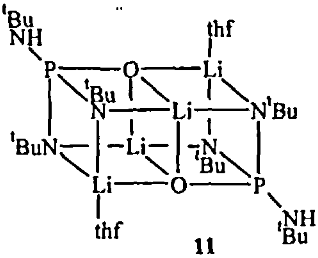

11

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