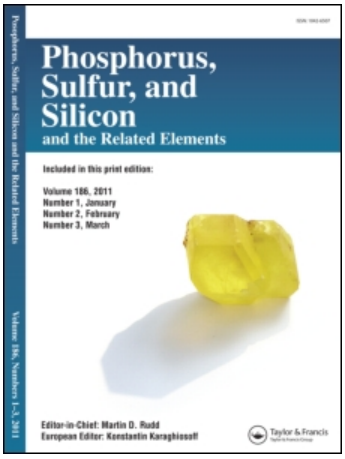

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RING AND CLUSTER STRUCTURES OF $\{Li[C(N^tBu)_2(HN^tBu)]\}_2 \cdot (THF)$ AND $\{Li_2[C(N^tBu)_3]\}_2$, CONTAINING THE NOVEL ANIONS $[C(N^tBu)_2(HN^tBu)]^-$ AND $[C(N^tBu)_3]^{2-}$

TRISTRAM CHIVERS and GABRIELE SCHATTE
Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada, T2N 1N4.

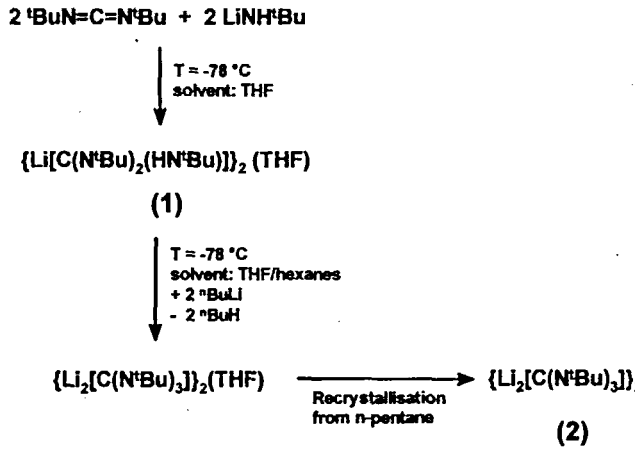
The reaction of *tert.*-butyl carbodiimide with one equivalent of $LiNH^tBu$ in tetrahydrofuran at -78 °C produces $\{Li[C(N^tBu)_2(HN^tBu)]\}_2 \cdot (THF)$ (**1**), which is an eight-membered $Li_2C_2N_4$ ring; the deprotonation of (**1**) with two equivalents of *n*-BuLi in tetrahydrofuran at -78 °C and recrystallisation of the product from *n*-pentane yielded the *unsolvated* dimer $\{Li_2[C(N^tBu)_3]\}_2$ (**2**), which adopts the structure of a distorted hexagonal prism.

Keywords: C-N-Li cluster, carbodiimides, hetero-trimethylene ligands

Recently there has been renewed interest in hetero-trimethylene ligands[1]. The first structural characterization of a triazatrimethylenemethane dianion $[C(NPh)_3]^{2-}$ in the tetrahydrofuran solvated complex $\{Li_4[C(NPh)_3]_2(thf)_6\}$ was reported in 1995[2]. It is prepared by the deprotonation of N,N',N"-triphenylguanidine. In an attempt to find a general route to heterotrimethylenemethane ligands of the type $[C(X)_2(Y)]^{2-}$ (X and Y = NR, O, S) we are investigating the

reaction of heteroallenes X=C=Y with LiHN^{t}Bu. Using a similar approach we were able to obtain the novel dianions $[E(N^tBu)_3]^{2-}$ (E = Se, Te) [3] by the reaction of the appropiate chalcogen diimide ^{t}BuN=E=N^{t}Bu with two molar equivalents of LiHN^{t}Bu.

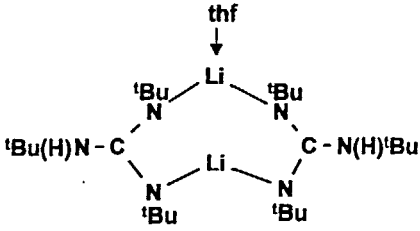
In contrast, the reaction of ^{t}BuN=C=N^{t}Bu with ^{t}BuNHLi produces $\{Li[C(NH^tBu)(N^tBu)_2]\}_2$(thf) (1) as the only product even when an excess of LiHN^{t}Bu is used (Scheme 1). The monoanion $[C(NH^tBu)(N^tBu)_2]^-$ can be deprotonated by n-BuLi in tetrahydrofuran and recrystallization of the product from *n*-pentane yielded the unsolvated complex $\{Li_2[C(N^tBu)_3]\}_2$ (2) (see Scheme 1).



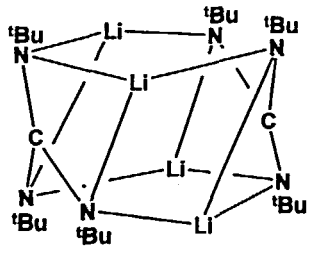
SCHEME 1

The crystal structure of (1) consists of two independent eight-membered $Li_2N_4C_2$ rings with twisted chair conformations, in which two $[C(N^tBu)_2(HN^tBu)]^-$ ions are bridged by two lithiums (see Fig. 1). The CN bond distances of 1.32(1) Å and of 1.37(1) Å in the $Li_2N_4C_2$

ring suggest a tendency toward CN double and CN single bonds, respectively, and limited delocalisation of negative charge. The exocyclic CN bond lengths of 1.39(1) Å are consistent with a C(sp^2)-N single bond and the presence of a hydrogen atom on the exocyclic nitrogen. Both two and three coordinate lithium ions are observed in this structure, with mean Li-N lengths of 1.97(2) (Li(4)/Li(2); coordinated to two nitrogens) and 2.03(2) Å (Li(3)/Li(1); coordinated two nitrogens and one THF molecule), respectively.



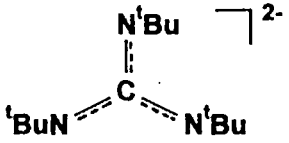
1



2

FIGURE 1 Schematic presentation of the structures of (**1**) and (**2**).

The identity of (**2**) was established by X-ray crystallography, which revealed a dimeric structure {Li$_2$[C(N^{t}Bu)$_3$]}$_2$. The unit cell consists of $C_2N_6Li_4$ cages (Fig.1). The mean C-N distance of 1.379(7) Å, which is comparable to the corresponding value of 1.36(1) Å found for {Li$_2$[C(NPh)$_3$]}$_2$(THF)$_6$ [2], is consistent with the resonance hybrid (**3**).



(3)

A detailed discussion of the results of the multinuclear NMR studies for both compounds can be found in ref. [4].

In summary, we have developed a potentially versatile route to triazatrimethylene methane dianions $C(NR)_3^{2-}$ from carbodiimides. The ligand chemistry of the dianion $[C(N^tBu)_3]^{2-}$ is currently under investigation.

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