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Reactions of *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane with butyllithium reagents

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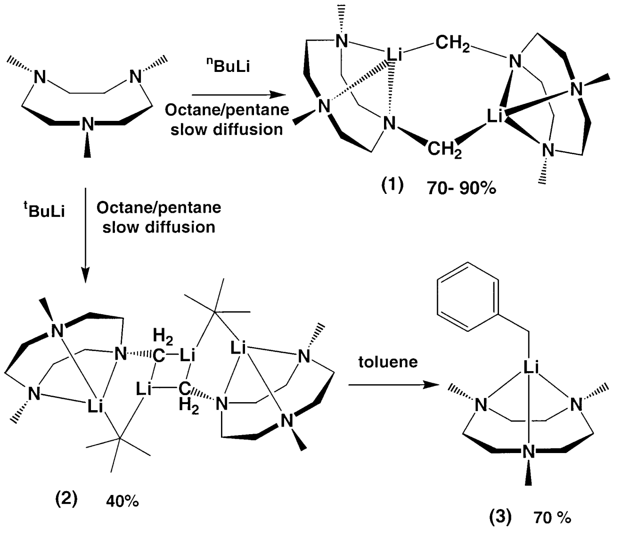
Treatment of *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane (Me_3tacn) with a range of alkyllithiums led to metallation of the N-methyl groups and, in the case of ^{t}BuLi, to the formation of an unusual μ-^{t}Bu complex; the latter undergoes clean transmetallation with toluene to form a Me_3tacn complex of benzyllithium.

As part of a study of the use of triazacyclononane (tacn) ligands in early transistion metal chemistry, we are developing new routes to functionalized tacn derivatives.[1] Given the propensity of cyclic polyamines to undergo heteroatom assisted metallation by reaction with alkyllithiums,[2] we turned our attention to reports of related reactions in tacn chemistry. In a pioneering study, Klumpp and coworkers showed using ^{6}Li NMR spectroscopy that the Me_3tacn was lithiated by the commonly used alkyllithium reagents such as ^{s}BuLi, ^{n}BuLi and ^{t}BuLi.[3] In addition, using ^{s}BuLi and ^{n}BuLi led to a dimeric structure in solution, whereas use of ^{t}BuLi gives rise to a ^{t}BuLi·Me_3tacn adduct. This difference in reactivity was attributed to whether or not a free, uncoordinated N-methyl amino group is present in solution, or whether all three nitrogen atoms are coordinated to lithium.

In attempts to exploit this chemistry on a synthetic level, we carried out a series of reactions with the aim of isolating and characterizing the products formed in solution. Here we describe the results of these experiments, which lead to some unusual structures in alkyllithium chemistry.

Conducting the reactions shown in Scheme 1 in a typical manner, *i.e.* in a stirred solution under anhydrous conditions, followed by attempted crystallization from a suitable solvent, were unsuccessful. Apparently, the species formed decomposed in solution at room temperature during the course of isolation (see below). With this in mind, we repeated the reactions under conditions aimed at maximizing the potential for formation of X-ray quality crystals directly from the reaction solution. The success of this technique obviously relies on the fact that the starting materials are soluble in the reaction solvent, but that the product, which is unstable in solution, is not; the latter is thereby removed as it is formed, without being given the opportunity to decompose.



Scheme 1

Introducing Me_3tacn in a narrow Schlenk tube and layering first by ^{n}octane, pentane and finally ^{n}BuLi in hexane, led after several days at −20 °C to pale yellow needles of compound **1** at the border between the layers in 70–90 % yield. The compound is pyrophoric and decomposes in a range of hydrocarbon and ethereal solvents. X-Ray diffraction analysis of **1** showed it to be the dimeric alkyl complex $[Me_2tacnCH_2Li]_2$ (see Fig. 1).†

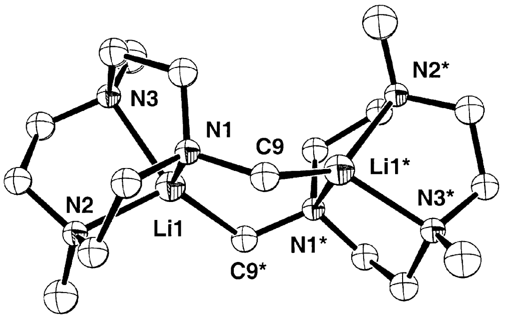


Fig. 1 ORTEP[17] view of **1** drawn with 30% probability ellipsoids.

The dimer resides on a crystallographic C_2-axis; its core consists of a six-membered, boat-configuration ring comprising Li(1), N(1), C(9),Li(1)*,N(1)* and C(9)*. Each lithium atom is coordinated by three nitrogen atoms from one tacn group and a methylene carbon atom from the second. The average Li–N bond lengths (av. 2.105 Å) are unexceptional[4] while the Li–C bond (2.080(1) Å) is relatively short in comparison to related parameters in known compounds (*e.g.* 2.207(4) Å in $[Li(CH_2NMe_2)(THF)]_4$[5]).

Repeating the experiment instead using ^{t}BuLi in ^{n}octane–pentane, afforded X-ray quality crystals of an extremely pyrophoric complex, **2** (Fig. 2).† Compound **2** is also dimeric, but the structure is quite different from **1**. It comprises a nearly planar four-membered Li_2C_2 ring (Li2, C9, Li3, C18) whose

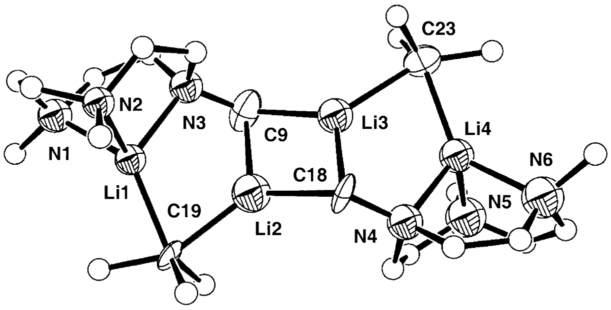


Fig. 2 ORTEP view of **2** drawn with 30% probability ellipsoids.

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midpoint is a non-crystallographic inversion center. The Li–C distances within the Li_2C_2-core are similar to related values in the literature.[5,6] In addition, the dimer incorporates two molecules of ${}^tBuLi$ in an unusual fashion: each quaternary ${}^tBu$-carbon (C19, C23) bridges two lithium atoms—one from the Li_2C_2 core and other (Li1/Li4) which is coordinated by the tacn moiety—in a relatively symmetrical fashion. The Li–C bond lengths (av. 2.2 Å) are similar to those in three other cases where a ${}^tBu$ group straddles two lithium atoms.[7–9] This coordination mode leads to two five-membered rings (Li2, C19, Li1, N3, C9; Li3, C23, Li4, N4, C18), that are arranged in an approximately envelope-conformation. Whereas Li1 and Li4 are tetrahedrally coordinated, Li2 and Li3 show a nearly perfect trigonal-planar coordination geometry, which is comparatively rare.[10–12] This is presumably due to the bulky ${}^tBu$-group, which shields the open coordination site, and to the lack of exogenous donor ligands.

The coordinative unsaturation present in **2** manifests itself in terms of reactivity in two ways. First, the compound is pyrophoric, and should thus be handled with care; second, it decomposes in non-aliphatic hydrocarbon or ether solvents. In one well-defined case, dissolution of **2** in toluene (Scheme 1) leads to a dark red solution from which, after several hours at −4 °C, pale yellow prisms of a new, much more stable lithium alkyl complex (**3**) were formed in high yield. This material is stable in solution and was obtained in pure form *via* recrystallization from pentane.

As shown by NMR spectroscopy and X-ray diffraction,‡ compound **3** is simply a benzyllithium complex with Me_3tacn. One of the two independent molecules in the unit cell is shown in Fig. 3. The lithium center Li1 is coordinated by the three nitrogens of the Me_3tacn and the benzylic carbon atom (C1) without any significant interaction to the phenyl ring. The coordination at Li is quite distorted from ideal tetrahedral angles due to the small bite angles from the Me_3tacn (angles between Li and the nitrogens are smaller than 90°). The Li–C bond lengths in the two molecules (2.18(2), 2.15(3) Å) are slightly shorter than in $LiCH_2Ph(tmeda)(thf)$ in which the corresponding parameter is 2.210(5) Å.[13] The Li–C–Ph angles are quite different in the two molecules of **3** (100.4(8) and 93.2(9)°), reflecting a substantial degree of flexibility in the Li–benzyl interaction.[14] (For comparison, the corresponding angle in $LiCH_2Ph(tmeda)(thf)$ is 94.6(2)°). This η^1-coordination of the Li atom to the benzyl ligand is obviously preferred if the coordination sites of lithium are blocked by strong N- or O-donors.[15,16]

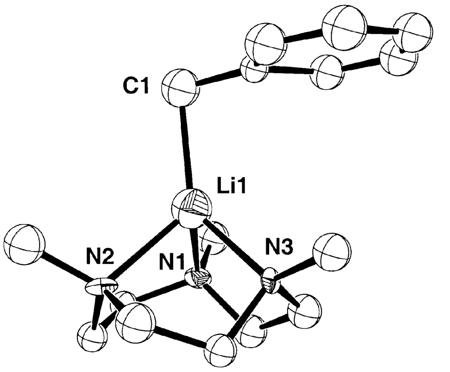

Fig. 3 ORTEP view of **3** drawn with 30% probability ellipsoids; only one of the two independent molecules is shown.

The reactivity of **3** is currently under investigation as are further studies to evaluate whether compound **1** may act as a synthon for the preparation of functionalized tacn ligands.

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Notes and references

† Attempts to characterize compounds **1** and **2** by spectroscopy or combustion analysis failed due to their decomposition in solution and their pyrophoric nature. For **3**: Yield 70%. C, H, N, analysis: found C, 71.01; H, 10.38; N, 15.35%. $C_{16}H_{28}LiN_3$ requires C, 71.35; H, 10.48; N, 15.60%. δ_H (25 °C, 500 MHz, C_6D_6): 7.11 (t, ${}^3J$ 7 Hz, 2H, *m*-Ar), 6.79 (d, ${}^3J$ 7 Hz, 2H, *o*-Ar), 6.25 (t, ${}^3J$ 7 Hz, 1H, *p*-Ar), 2.31 (s, 2H, CH_2), 2.04 (s, 9H, CH_3) 1.70 (m,12H, NCH_2); δ_C (25 °C, 126 MHz, C_6D_6): 160.0 (*i*-C), 129.5 (*m*-C), 116.5 (*o*-C), 105.6 (*p*-C), 53.0 (CH_2), 45.4 (CH_3), 35.9 (NCH_2); δ_{Li} (25 °C, 194 MHz, C_6D_6, 3 M LiCl in D_2O as external standard): 2.04 (s).

‡ The lack of heavy atoms and the instability of the compounds led to collection of a limited number of data; this precluded anisotropic refinement of most atoms in all three structures.

Crystal data for **1**: $C_9H_{20}LiN_3$, $M = 177.22$, tetragonal, $a = 12.288(1)$, $c = 14.407(2)$ Å, $V = 2175.5(3)$ Å^3, $T = 169$ K, space group $\bar{P}_42_1c$ (no. 114), $Z = 8$, μ(Mo-Kα) = 0.65 cm^{-1}, 9830 reflections measured, 1199 unique ($R_{int} = 0.053$), $D_{calc} = 1.082$ g cm^{-3}, $R = 0.042$, $R_w = 0.039$.

For **2**: $C_{13}H_{29}Li_2N_3$, $M = 241.27$, orthorhombic, $a = 18.785(4)$, $b = 14.607(3)$, $c = 23.964(5)$ Å, $V = 6575(1)$ Å^3, $T = 121$ K, space group *Pbca* (no. 61), $Z = 16$, μ(Mo-Kα) = 0.56 cm^{-1}, 21445 reflections measured, 3872 unique ($R_{int} = 0.092$), $D_{calc} = 0.975$ g cm^{-3}, $R = 0.142$, $R_w = 0.170$.

For **3**: $C_{16}H_{28}LiN_3$, $M = 269.36$, monoclinic, $a = 17.075(4)$, $b = 12.258(3)$, $c = 16.533(4)$ Å, $V = 3341(2)$ Å^3, $T = 153$ K, space group $P2_1/c$ (no. 14), $Z = 8$, μ(Mo-Kα) = 0.63 cm^{-1}, 12166 reflections measured, 4322 unique ($R_{int} = 0.066$), $D_{calc} = 1.071$ g cm^{-3}, $R = 0.069$, $R_w = 0.090$. The structure was initially solved and refined with $c' = ½c$. Using this halved unit cell leads to an acceptable solution, but while the "tacn" part of the molecule is well defined, the benzyl group position was disordered over two sites. Doubling the unit cell resulted in two well-ordered independent molecules differing only in the orientation of the benzyl group. We, therefore, concluded that the apparent translational symmetry in the "large" unit cell is just pseudo-symmetry. CCDC reference numbers 185955–185957. See http://www.rsc.org/suppdata/dt/b2/b205792c/ for crystallographic data in CIF or other electronic format.

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