X-Ray Crystal and Molecular Structure of Hexameric Di-t-butylmethyleneaminolithium, $(LiN{=}CBu^t_2)_6$: Electron-deficient Bridging of Li_3 Triangles by Methyleneamino Nitrogen Atoms

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Summary An *X*-ray crystallographic study of the title compound, $(LiN{=}CBu^t_2)_6$, has revealed a 'folded chair' arrangement of its metal atoms held together by triply bridging methyleneamino groups in what is believed to be the first example of electron-deficient bridging through the nitrogen atom of an organonitrogen ligand.

WHEREAS electron-deficient bridging of pairs or triangles of metal atoms by *C*-attached organic groups is an established feature of the organometallic chemistry of such metals as lithium, beryllium, magnesium, and aluminium,[1,2] bridging of these same metals by *N*-attached organic groups, *e.g.* amino groups NR_2[3,4] or methyleneamino groups $N{=}CR_2$[1,5-7]

is normally electron-precise in that the number of bonding contacts is equal to the number of electron pairs available for bonding. We report here what is believed to be the first example of electron-deficient bonding by a nitrogen-attached ligand, revealed by an *X*-ray crystallographic study of di-t-butylmethyleneaminolithium, $LiN{=}CBu^t_2$, a compound that has been used as a reagent for preparing di-t-butylmethyleneamino derivatives of various metals and metalloids.[5–8]

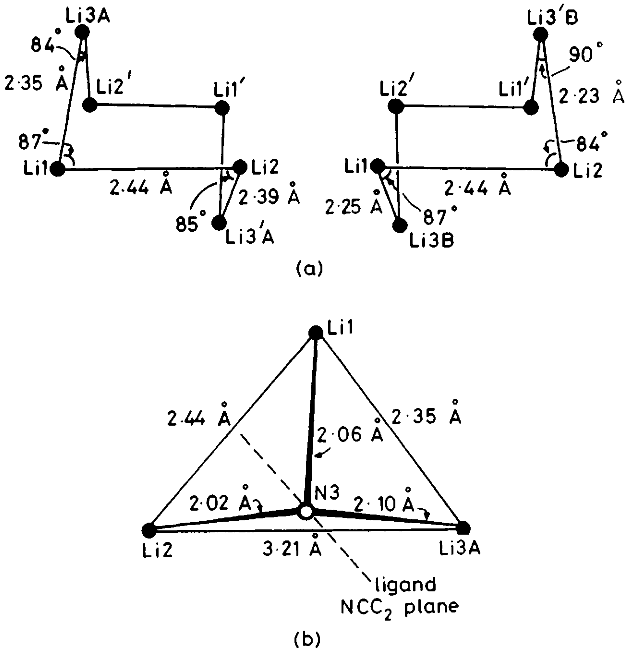

FIGURE. (a) The two possible orientations of the centrosymmetric chair-shaped Li_6 ring of $(LiN{=}CBu^t_2)_6$, showing interatomic distances (mean e.s.d. 0·03 Å) and angles (mean e.s.d. 1·5°). (b) The type of bridging of an Li_3 face by a μ^3-methyleneamino group that occurs in $(LiN{=}CBu^t_2)_6$, exemplified by the face Li1, Li2, Li3A.

A sample of $LiN{=}CBu^t_2$ was prepared from equimolar proportions of Bu^tCN and $LiBu^t$ in hexane,[8] and recrystallised from hexane as very pale yellow, transparent, moisture-sensitive monoclinic plates (found: C,72·7; H, 13·2; Li, 4·6; N, 9·5%. $C_9H_{18}LiN$ requires C, 73·5; H, 12·2; Li,4·8; N, 9·5%) with a = 12·429(1), b = 20·794(2), c = 13·099(1) Å, β = 116·78(2)°, D_c = 0·970, D_m = 0·98 g cm^{-3}, Z = 2 formula units, μ = 0·27 cm^{-1} for Mo-K_α radiation, space group $P2_1/c$. The intensities of the hkl and $\bar{h}kl$ reflections were measured on a Hilger and Watts four-circle diffractometer using Zr-filtered radiation and a 2θ–θ scan. The data were corrected for Lorentz and polarisation effects and for absorption. A total of 2817 unique reflections was obtained, of which 1625 were classed as observed, having net counts $\geqslant 2\sigma$.†

The hexameric structure, features of which are shown in the Figure, was solved by the symbolic addition procedure using a multi-solution programme. Disordering or extensive libration of some of the t-butyl groups prevented location of the hydrogen atoms and accounts for the rather high final *R*-value (0·16) obtained. During refinement, alternative positions (3A and 3B) were found for one of the three lithium atoms in the asymmetric unit $(LiN{=}CBu^t_2)_3$. These were assigned site occupation factors of 0·5, and correspond to two possible orientations of the slightly folded chair-shaped Li_6 rings. The mean dihedral angle between the chair seat and back is 85°. The $N{=}CBu^t_2$ ligands bridge the six smaller of the eight triangular faces of the Li_6 core, orientated so that the ligand NCC_2 planes are perpendicular to the bridged Li_3 faces. Each bridged Li_3 face has one long edge [ranging in length from 3·13(5)—3·31(4) Å, mean 3·21(1) Å] and two short edges [ranging in length from 2·23(5)—2·44(3) Å, mean 2·35(1) Å], one roughly parallel to the ligand NCC_2 plane, the other perpendicular to and roughly bisected by that plane. The bridging nitrogen atoms are approximately equidistant from the three bridged metal atoms; the Li–N distances range from 1·97(3)—2·19(3) Å, mean 2·06(1) Å, *cf.* 2·00 Å in $[LiN(SiMe_3)_2]_3$.[9]

This type of ring is not unprecedented in lithium chemistry. The Li_6N_6 skeleton resembles surprisingly closely the Li_6C_6 and Li_6Si_6 skeletons of the hexamers $[Li(cyclohexyl)]_6$[10] and $(LiSiMe_3)_6$,[11] even though $(LiN{=}CBu^t_2)_6$ contains twice as many skeletal bonding electrons (12 pairs) as the other compounds (6 pairs). We assume that each methyleneamino group acts as a 3-electron ligand. In principle, by using N=C π-bonding electrons, it might function as a 5-electron ligand, leading to a total of 18 skeletal bond pairs for the hexamer, though the orientation of the ligands, and the apparently normal length of their N=C double bonds [1·30(1) Å], seem to rule this out. The hexamer $(LiN{=}CBu^t_2)_6$ thus contains only twelve skeletal bond pairs to allocate to its eighteen Li–N skeletal bonds, or to a total of twenty-four skeletal bonds if the short Li · · · · Li contacts are included. Their length, 2·35(1) Å, suggests that they should be included, as they appear to be the shortest Li · · · · Li links yet reported; *cf.* 2·40 Å in $[Li(cyclohexyl)]_6$,[10] 2·42 in $(LiEt)_{4n}$,[12] 2·68 in $(LiMe)_4$,[13] 2·70 in $(LiSiMe_3)_6$,[11] and 2·74 in the $Me_2NCH_2CH_2NMe_2$ adduct of bicyclobutyl-lithium.[14] The Li · · · · Li distance in the metal is 3·04 Å.[15]

The type of bridging by nitrogen that we have found in $(LiN{=}CBu^t_2)_6$ provides the link that was previously missing between the well-established bridging of Li_3 triangles by *C*-attached alkyl groups in lithium alkyls,[10,12–14] and the bridging of Li_4 squares by the oxygen atoms of the methoxy groups in LiOMe.[16] All three bridge types are electron-deficient in that they have more bonding contacts than bond pairs.

The hexameric molecules present in crystalline $LiN{=}CBu^t_2$ apparently do not persist in solution. Cryoscopic studies on benzene solutions indicate the presence of dimers

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

$(LiN{=}CBu^t_2)_2$ (M, found 260; required 294) for which an electron-precise $(LiN)_2$ ring structure appears likely.

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