Lithium Tetrakis(di-t-butylmethyleneamino)aluminate

By H. M. M. SHEARER, R. SNAITH, J. D. SOWERBY, and K. WADE*

(*Chemistry Department, Durham University, South Road, Durham*)

Summary The compound $\mathrm{LiAl(N:CBu^t_2)_4}$, prepared from $\mathrm{AlCl_3 + 4\,Bu^t_2C:NLi}$, has been shown by *X*-ray diffraction to contain an aluminium atom surrounded by a distorted tetrahedron of di-t-butylmethyleneamino-groups, two terminally attached, with the near-linear C:NAl skeletons and short Al–N distances appropriate for appreciable $\mathrm{N}\rightleftharpoons\mathrm{Al}$ ($p \rightarrow d$) dative π-bonding, the other two bridging the aluminium to the lithium, which is also apparently involved in a novel type of Li · · · H–C interaction.

LARGELY on the basis of their high azomethine stretching frequencies, several species $\mathrm{R_2C:NMX_2}$ (M = Be,[1] B,[2-4] C,[5] or Al[6]) containing three-co-ordinate M have been assigned the pseudo-allene structures appropriate for appreciable $\mathrm{N}\rightleftharpoons\mathrm{M}$ ($d \rightarrow p$) dative π-bonding, and confirmed recently for $\mathrm{Ph_2C:NBmesityl_2}$ by *X*-ray crystallography.[7] We here describe the new compound $\mathrm{LiAl(N:CBu^t_2)_4}$, which also has a high-frequency (1700 cm^{-1}) azomethine stretching absorption and which contains ketimino-groups $\mathrm{Bu^t_2C:N}$– terminally attached to four-co-ordinate aluminium by near-linear C:NAl units, as appropriate for appreciable $\mathrm{N}\rightleftharpoons\mathrm{M}$ ($p \rightarrow d$) dative π-bonding.

The pale yellow, moisture-sensitive compound, prepared from $\mathrm{AlCl_3 + 4Bu^t_2C:NLi}$ in a hexane–ether mixture, was recrystallized from pentane, hexane, or toluene, and identified by full elemental analysis. It is monomeric in the gas phase (by mass spectroscopy), in benzene solution (by cryoscopy), and in the crystal (by *X*-ray diffraction). Crystals were sealed under dry nitrogen in glass-walled capillaries: $a = 17{\cdot}098$, $b = 15{\cdot}011$, $c = 15{\cdot}912$ Å, $U = 4084$ Å^3, $Z = 4$, $D_m = 0{\cdot}96$ (by flotation), $D_c = 0{\cdot}96$ g cm^{-3}, space group *Pnna*. Three-dimensional *X*-ray data were collected on a Hilger and Watts automatic four-circle diffractometer using Mo-K_α radiation. Altogether 1917 independent reflections were measured (to $2\theta = 40°$) of which 1269 were judged to be observed. The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-square techniques, and finally by full-matrix methods, to $R = 0{\cdot}108$.

The molecule (see Figure) has a two-fold symmetry axis through the metal atoms, which are bridged by two of the ketimino-groups, the remaining two ketimino-groups being terminally attached to the aluminium atom by short Al–N bonds and a large Al–N(1)–C(1) bond angle, as appropriate for considerable $\mathrm{N}\rightleftharpoons\mathrm{Al}$ ($p \rightarrow d$) dative π-bonding [*cf.* $\mathrm{Al}\leftrightharpoons\mathrm{N}$ bond lengths of 1·78 Å in $\mathrm{[(Me_3Si)_2N]_3Al}$[8] and 1·79 Å in $\mathrm{Al_4Cl_4(NMe_2)_4(NMe)_2}$,[9] and contrast *ca.* 1·94 Å for Al–N single bonds[9,10]]. A lesser, though still apparently significant, degree of $\mathrm{N}\rightleftharpoons\mathrm{Al}$ ($p \rightarrow d$) dative π-bonding is unexpectedly indicated by the comparative shortness of the *bridging* Al–N(2) bonds [*cf.* 1·96 Å for the bridging Al–N bonds of $\mathrm{(Me_2AlNMe_2)_2}$,[11] and 1·94 Å for the bridging Al–N bonds of $\mathrm{(Bu^tCMe:NAlMe_2)_2}$][12] and by the large angle Al–N(2)–C(2). The $\mathrm{AlN_2Li}$ ring geometry is also unusual in its short Li · · · Al distance [2·55(4) Å] and small Li–N(2)–Al angle (84°). A particularly acute angle at the bridging non-metal atom and a short metal · · · metal distance are normally found in systems with electron-deficient bridges,[13] as in $\mathrm{LiAlEt_4}$,[14] for which the Li–Al distance is 2·71 Å, and the angle Li–C–Al is 77°. The Li–N(2) bridging bonds are of a length appropriate for essentially single bonds.

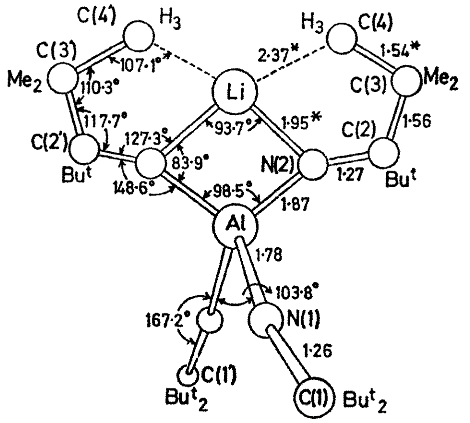

FIGURE. *Molecular structure of* $\mathrm{LiAl(N:CBu^t_2)_4}$; *interatomic distances in Å; e.s.d.'s as follows;* 0·02*Å for distances marked**, 0·01*Å for remainder; for all angles, e.s.d.'s are less than* 1°.

The large bridging Al–N(2)–C(2) angle means that one t-butyl group of each bridging $\mathrm{Bu^t_2C:N}$– unit leans towards the lithium atom. Although in principle free rotation about the $\mathrm{Bu^t}$–C bond can occur, and there would be room for the butyl group to be so orientated that its methyl groups did not point towards the lithium, nevertheless one methyl carbon, C(4), adopts a position *as close as possible to the lithium* bearing in mind that carbon, C(4), is at a normal single-bond distance from C(3). The Li–C(4) distance of

2·37 Å is little longer than the Li–C distance of 2·31 Å in $(MeLi)_4$.[15] Although the positions of the hydrogen atoms could not be found, the position of carbon C(4) is such that the most probable orientation of its three hydrogen atoms will place two of them effectively in bridging positions between the carbon and the lithium. The ^1H n.m.r. spectrum of $LiAl(N{:}CBu^t_2)_4$ in toluene was too complex to show unambiguously whether any lithium–hydrogen interactions persist in solution.

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