Synthesis and Crystal Structure of Bicyclo[1,1,0]butan-1-yl-lithium–Tetramethylethylenediamine

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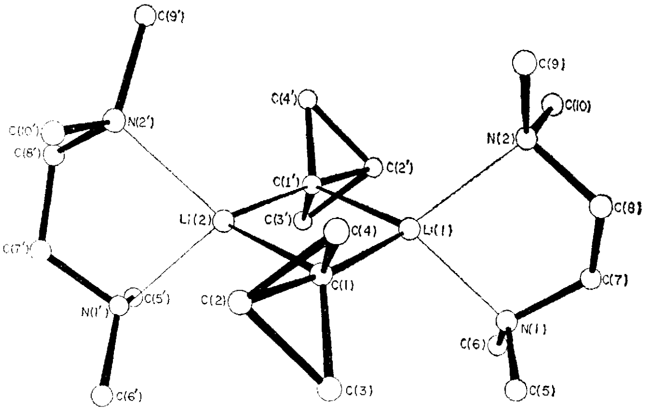
Summary The crystal structure of bicyclo[1,1,0]butan-1-yl-lithium–tetramethylethylenediamine (TMEDA) was determined and found to consist of dimeric units consisting of two lithium atoms bridged by two bicyclobutyl groups and a TMEDA molecule co-ordinated to each lithium atom.

Electron deficient compounds have been reported with bridging primary and secondary alkyl,[1,2] allyl,[3] phenyl,[4] and acetylenic[5] groups, however, there have been no reported examples of well characterized tertiary carbon electron deficient systems. We report the isolation and structural characterization of a system containing a bicyclo[1,1,0]butyl bridging group.

Bicyclobutane[6] was first vacuum distilled into a flask containing hexane at dry ice temperature, then allowed to warm to 0 °C under N_2. An equimolar amount of Bu^nLi in hexane was added at 0 °C by an air-tight syringe followed by a slight excess of tetramethylethylenediamine (TMEDA). Evaporation of the hexane and filtration yielded colourless crystals which were recrystallized from benzene. *Crystal data:* Space group monoclinic, $C2/m$; $a = 8{\cdot}95 \pm 0{\cdot}01$ Å, $b = 15{\cdot}05 \pm 0{\cdot}03$ Å, $c = 9{\cdot}38 \pm 0{\cdot}01$ Å, $\beta = 97{\cdot}90°$; $U = 1251{\cdot}4$ Å^3; $D_c = 0{\cdot}9352$ g cm^{-3} for four monomeric units. The $N(Z)$ test[7] indicated a centric distribution of data. Refinement on 337 reflections with $I \geqslant 2\sigma(I)$ using anisotropic temperature factors for the non-hydrogen atoms and a disordered model for the carbon atoms of the TMEDA molecule in the space group $C2/m$ has given an R-factor of 10·8%. Refinement (non-disordered) was tried also in the space groups $C2$ and Cm, but both Fourier and least-squares analyses led again to the disordered model.



Figure

Bicyclo[1,1,0]butanyl-lithium–TMEDA is dimeric (Figure) with two lithium atoms, bridged by two bicyclobutanyl groups bonded through the bridgehead carbon atoms and possesses crystallographic symmetry $C_{2h}(2/m)$. The disorder of the TMEDA carbon atoms takes the same form as that found for triphenylmethyl-lithium–TMEDA.[8] Only one conformation of each disordered TMEDA molecule is shown for simplicity. The nitrogen atoms of a TMEDA molecule are co-ordinated to each lithium atom in such a way as to form a distorted tetrahedral arrangement around each lithium atom. To our knowledge, this structure is the first example of a dimeric lithium–carbon–lithium electron deficient compound and the first example of a tertiary carbon deficient compound. The fact that a tertiary carbon can participate in electron deficient bonding supports the view that hydrogen atoms are not an integral part of the bonding in metal–

carbon–metal bridge bonds. Hydrogen atom involvement was proposed for the trimethylaluminium dimer,[9] but was subsequently refuted.[10]

The average bridgehead carbon–lithium bond length is 2·23(5) Å. In comparison, ethyl-lithium[11] has Li–C bond lengths of 2·19 Å and 2·25 Å, average value 2·22 Å. The lithium–lithium atom distance within the dimer is 2·74(7) Å, *ca.* twice the covalent radius for lithium. This is longer than the lithium–lithium distances in methyl-lithium[12] (2·56 Å) and in ethyl-lithium[11] (2·42 Å, 2·60 Å, and 2·63 Å) which are both tetramers. The angles C(1)–Li(1)–C(1′) and Li(1)–C(1)–Li(2) are 104(2)° and 76(2)° respectively and are consistent with those found for other electron deficient compounds.[1] The Li–N distances are 2·05(3) Å with a N–Li–N bond angle of 84(2)°.

The above compound provides a convenient starting point for the synthesis of other organometallic compounds containing a bicyclo[1,1,0]butanyl group. The synthesis and characterization of bisbicyclobutylmercury has been completed and will be reported in a later publication.

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