Different donor binding modes of the pincer ligand 2,6-bis[(diethylamino)methyl]phenyl: intermolecularly chelating in $Li[2,6-(NEt_2CH_2)_2C_6H_3]$ and both mono- and bi-dentate in $BCl_2\{2-[BCl_3(NEt_2CH_2)]-6-(NEt_2CH_2)C_6H_3\}$

Robert Schlengermann, Joachim Sieler, Svea Jelonek and Evamarie Hey-Hawkins*

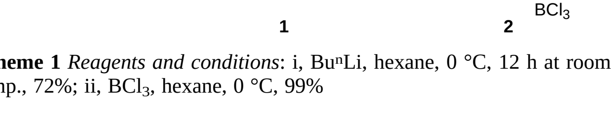
Institut für Anorganische Chemie der Universität Leipzig, Talstrasse 35, D-04103 Leipzig, Germany

The reaction of dimeric $Li[2,6-(NEt_2CH_2)_2C_6H_3]$ 1 with BCl_3 yields $BCl_2\{2-[BCl_3(NEt_2CH_2)]-6-(NEt_2CH_2)C_6H_3\}$ 2, independent of the stoichiometric ratio (1 : 1 or 1 : 2) or reaction conditions (0 °C or boiling hexane).

The lithium derivatives of monoanionic terdentate ligands $2,6-(NR_2CH_2)_2C_6H_3$ (R = Me, Et) are valuable starting materials for the preparation of transition-metal or main-group element derivatives.[1] A variety of binding modes to late transition metals, *i.e.* as two-, four- and six-electron donor, have been observed.[2] Intramolecular coordination of the amino group strongly stabilises these compounds.[2] Thus, the intramolecularly stabilised five-coordinate 2,6-[bis(dialkylamino)-methyl]phenyl derivatives $AlX_2[2,6-(NMe_2CH_2)_2C_6H_3]$ (X = Cl, H),[3] $GaMe_2[2,6-(NMe_2CH_2)_2C_6H_3]$,[4] $InCl_2[2,6-(NEt_2CH_2)_2C_6H_3]$,[5] $InMe(Cl)[2,6-(NEt_2CH_2)_2C_6H_3]$,[5] $InEt_2-[2,6-(NEt_2CH_2)_2C_6H_3]$[4] and $InR_2[2,6-(NMe_2CH_2)_2C_6H_3]$ (R = Me, Et, Pr),[4] are liquids or low-melting solids and far less air-sensitive than trimethyl compounds; they are therefore suitable replacements for MOVPE.[4,5] Of the boron analogues, only the boronic acid derivative $B(OH)_2[2,6-(NMe_2CH_2)_2C_6H_3]$[6] and the boronates $B(OCH_2CR_2O)[2,6-(NMe_2CH_2)_2C_6H_3]$ (R = H, Ph),[7] $B(OCH_2CMe_2CH_2O)[2,6-(NMe_2CH_2)_2C_6H_3]$[8] and $B(OCH_2CHMeO)[2,6-(NMe_2CH_2)_2-C_6H_3]$,[8] which were synthesised from boronic acid and diols, have been reported in the literature. Since base-stabilised arylboron dichloride derivatives would appear to be useful starting materials for the preparation of transition-metal boranediyl complexes,[9] we attempted the preparation of these compounds.

The synthesis and *in situ* reactions of $Li[2,6-(NEt_2CH_2)_2C_6H_3]$ **1** have been reported.† **1** (2.0 g, 7.8 mmol) reacts with $BCl_3(OEt_2)$ (15.6 mmol) in hexane (25 ml) at 0 °C to give $BCl_2\{2-[BCl_3(NEt_2CH_2)]-6-(NEt_2CH_2)C_6H_3\}$ **2** in almost quantitative yield, independent of the stoichiometric ratio or reaction conditions (Scheme 1); formation of a BCl_3-free product was not observed. This suggests that **2** is the thermodynamically favoured product. In the comparable reaction of **1** with $InCl_3$, $InCl_2[2,6-(NEt_2CH_2)_2C_6H_3]$ is obtained, in which both amino groups are coordinated to the In atom.[5]

In addition to being indispensable reagents for preparative organometallic and organic chemistry, lithium compounds often exhibit fascinating structures in the solid state.[10] In the compounds studied up to now, the Li atom exhibits a pronounced tendency to interact with electron-rich ligands or donor molecules, or aggregation through electron-deficient Li–C bonds is observed, leading to a large variety of structures.[10] A general principle for the dimerisation of lithium reagents has been described in the literature.[11]



Scheme 1 *Reagents and conditions*: i, Bu^nLi, hexane, 0 °C, 12 h at room temp., 72%; ii, BCl_3, hexane, 0 °C, 99%

In the solid state $Li[2,6-(NEt_2CH_2)_2C_6H_3]$ **1** consists of dimeric units in which the Li atoms are bonded to the two *ipso*-C atoms of the aryl rings by three-centre–two-electron bonds; the molecule has C_2 symmetry (Fig. 1).‡ The tetrahedral coordination of Li is completed by intra- and inter-molecular interactions with one amino group of each aryl ligand. The *ipso*-C atoms, C(1) and C(10), have tetrahedral rather than planar geometry. The structural parameters of **1** are in agreement with those of other structurally characterised dimeric lithium aryls.[12]§ The structural data [Li–C, Li···Li, Li–N, bite angle N(2)–Li(1)–C(10) and N(1)–Li(1)–C(1)] as well as the overall structure (C_2 symmetry) and geometry of **1** [angle between planes C(1)–C(2a)/C_2Li_2 56.8(1)°, C(10)–C(14a)/C_2Li_2 56.9(2)°, C(1)–C(2a)/C(10)-C(14a) 66.20(8)°] are nearly identical to those of dimeric {2,3,5,6-tetrakis-[(dimethylamino)methyl]phenyl}lithium.[13] Other related lithium derivatives with two intra- and inter-molecularly chelating *ortho* substituents are tetrameric $Li[2-(NMe_2CH_2)C_6H_4]$[14] and $Li[2,6-(NMe_2CH_2)_2C_6H_3]$,[6,14] which is dimeric according to a molecular mass determination.

Like $\{Li[2,6-(NMe_2CH_2)_2C_6H_3]\}_2$,[14] dimeric **1** has C_2 symmetry. Therefore the C–CH_2-N and CH_2CH_3 groups are

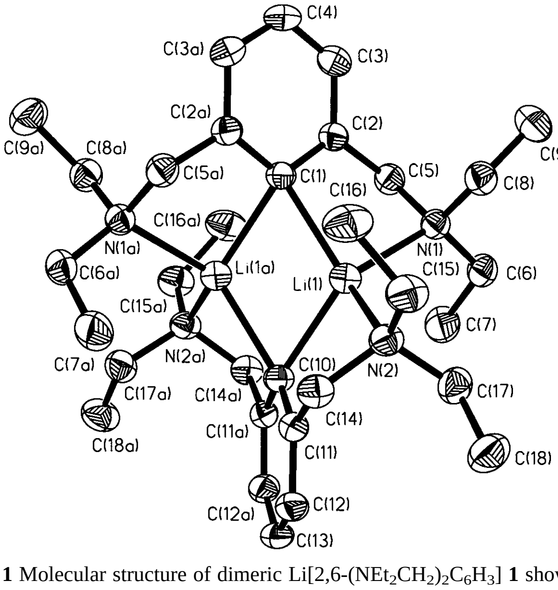


Fig. 1 Molecular structure of dimeric $Li[2,6-(NEt_2CH_2)_2C_6H_3]$ **1** showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP).[18] Selected bond lengths (Å) and angles (°): Li(1)–N(1) 2.178(3), Li(1)–N(2) 2.164(3), Li(1)–C(1) 2.228(3), Li(1)–C(10) 2.231(3), Li(1)···Li(1a) 2.483(5); N(2)–Li(1)–N(1) 111.01(12), N(2)–Li(1)–C(1) 134.67(13), N(1)–Li(1)-C(1) 86.07(10), N(2)–Li(1)–C(10) 85.92(10), N(1)–Li(1)–C(10) 134.27(13), C(1)–Li(1)–C(10) 112.32(12), Li(1)–C(1)–Li(1a) 67.73(14), Li(1)–C(10)–Li(1a) 67.62(14), C(2)–C(1)–C(2a) 114.9(2), C(11)–C(10)–C(11a) 114.4(2).

diastereotopic (below 16 °C); above 16 °C they become homotopic as the molecule becomes fluctional ($\Delta G^{\ddagger} = 54.6 \pm 0.2$ kJ mol^{-1}).[15]¶

Crystals of **2** were obtained from dichloromethane at −25 °C. The molecular structure of **2** is shown in Fig. 2.‡ In **2**, an arylboron dichloride is intramolecularly stabilised by interaction with one amino group, giving a five-membered B–C–C–C–N ring (BC_3 coplanar, N lies 0.5 Å below this plane). This leads to a distorted tetrahedral environment at B(1) [small C(1)–B(1)–N(2) bite angle and large C(1)–B(1)–Cl(1) bond angle]. The structural data of the C–C–C–N–B five-membered ring in **2** are similar to those of $B(OCH_2CPh_2O)[2,6\text{-}(NMe_2CH_2)_2C_6H_3]$.[7] Due to the coordination number of five in $InMe(Cl)[2,6\text{-}(NEt_2CH_2)_2C_6H_3]$, the C–In–N bite angles are even smaller [72.7(1), 72.3(1)°][5] than in **2** and the boronate. It is well known that BCl_3 forms stable adducts with ethers and amines, and the geometry of the BCl_3 group which is coordinated by the second amino group in **2** is comparable to that of undistorted tetrahedral $BCl_3(NMe_3)$.[16] To our knowledge, **2** is the first example where the pincer ligand $2,6\text{-}(NEt_2CH_2)_2C_6H_3$ acts as a monodentate ligand towards one molecule and as a bidentate ligand towards another. The only remotely related example is $[WL(CO)_3(NCMe)]$ [L = $2\text{-}Ph_3SnC_6H_4CH_2N(Me)CH_2CH_2NMe_2$], in which L exhibits η^2-N,N′ coordination to W and η^1-C coordination to Sn.[17]

While the related boronates $B(OCH_2CR_2O)[2,6\text{-}(NMe_2CH_2)_2C_6H_3]$ (R = H, Ph) are dynamic in solution due to facile exchange of amine ligands,[7] in **2** this process is not possible due to the coordination of one amino group to the $(aryl)BCl_2$ fragment, while the other is coordinated to a BCl_3 molecule. Thus, in the proton NMR spectrum of **2** (in $[^2H_8]$thf),¶ the non-equivalence of the CC*HH*N (AB system) and NC*HH*CH_3 protons (one q for each H of both methylene groups) indicates that the five-membered chelate ring C–C–C–N–B is rigid in solution. For the $C\text{-}CH_2N(BCl_3)(CH_2CH_3)_2$ group, these are equivalent (one s, one q). The chemical shifts and coupling patterns are solvent dependent.¶

The results presented here show that $Li[2,6\text{-}(NEt_2CH_2)_2C_6H_3]$ **1** is dimeric in the solid state with C_2 symmetry. The reaction of **1** with BCl_3 yields the novel donor-stabilised arylboron dichloride, $BCl_2\{2\text{-}[BCl_3(NEt_2CH_2)]\text{-}6\text{-}(NEt_2CH_2)C_6H_3\}$ **2**; a BCl_3-free compound was not obtained. We are presently investigating the chemistry of **2** and its use in the preparation of transition-metal boranyl or boranediyl complexes.

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (R. S.) and the Fonds der Chemischen Industrie; the company Chemetall GmbH has provided a generous donation of lithium alkyls, and Hoechst AG a generous donation of chemicals.

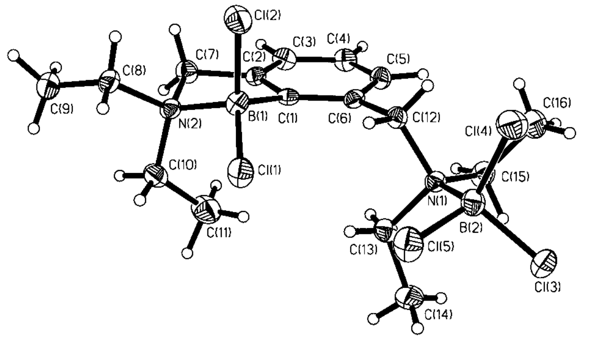


Fig. 2 Molecular structure of $BCl_2\{2\text{-}[BCl_3(NEt_2CH_2)]\text{-}6\text{-}(NEt_2CH_2)C_6H_3\}$ **2** showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL PLUS; XP).[18] Selected bond lengths (Å) and angles (°): B(1)–Cl(1) 1.842(4), B(1)–Cl(2) 1.882(5), B(2)–Cl(3) 1.855(5), B(2)–Cl(4) 1.852(5), B(2)–Cl(5) 1.841(5), B(1)–N(2) 1.649(5), B(2)–N(1) 1.639(5), B(1)–C(1) 1.598(5); C(7)–N(2)–B(1) 103.3(3), C(1)–B(1)–N(2) 100.5(3), C(2)–C(1)–C(6) 119.1(3), C(2)–C(1)–B(1) 107.7(3), C(6)–C(1)–B(1) 132.1(3).

Footnotes

† $Li[2,6\text{-}(NEt_2CH_2)_2C_6H_3]$ **1** was prepared according to the literature procedure.[4,5] Recrystallisation from hexane gave colourless crystals (72%).

‡ *Crystal data*: for **1**: $C_{32}H_{54}Li_2N_4$, $M = 508.68$, white crystals, 0.5 × 0.5 × 0.5 mm, orthorhombic, space group *Pbcn* (no. 60), $T = 200(2)$ K, $a = 13.4959(9)$, $b = 16.9164(11)$, $c = 14.1022(9)$ Å, $U = 3219.6(4)$ Å^3, $Z = 4$, $D_c = 1.049$ g cm^{-3}, $F(000) = 1120$, μ(Mo-Kα) = 0.060 mm^{-1}, 13028 reflections collected with $2 < \theta < 26°$; of these 2956 were independent; 283 parameters, refinements converge to $R_1 = 0.0477$, $wR_2 = 0.1004$ [for reflections with $I > 2\sigma(I)$], $R_1 = 0.0656$, $wR_2 = 0.1123$ (all data). **2**: $C_{16}H_{27}B_2Cl_5N_2$, $M = 446.27$, white crystals, 0.15 × 0.10 × 0.10 mm, triclinic, space group $P\bar{1}$ (no. 2), $T = 260(2)$ K, $a = 7.069(2)$, $b = 10.837(5)$, $c = 14.090(5)$ Å, $\alpha = 90.09(2)$, $\beta = 104.16(2)$, $\gamma = 97.35(2)°$, $U = 1037.3(7)$ Å^3, $Z = 2$, $D_c = 1.429$ g cm^{-3}, $F(000) = 464$, μ(Mo-Kα) = 0.702 mm^{-1}, 4656 reflections collected with $1.5 < \theta < 26°$; of these 3409 were independent; 334 parameters, refinements converge to $R_1 = 0.0460$, $wR_2 = 0.0889$ [for reflections with $I > 2\sigma(I)$], $R_1 = 0.0752$, $wR_2 = 0.1082$ (all data).[18] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/315.

§ In a structurally characterised dimeric aryllithium, Li–C ranges from 2.19 to 2.28 Å, Li···Li from 2.37 to 2.66 Å, and Li–C–Li from 64.2 to 67.4°.[14]

¶ Full spectroscopic discussion will be given in the full paper.

References

1 A. A. H. van der Zeijden and G. van Koten, *Inorg. Chem.*, 1986, **25**, 4723; A. L. Wayda and R. D. Rogers, *Organometallics*, 1985, **4**, 1440; F. A. Cotton and G. N. Mott, *Organometallics*, 1982, **1**, 38; L. E. Manzer, *J. Am. Chem. Soc.*, 1978, **100**, 8068; and references therein.

2 G. van Koten, *Pure Appl. Chem.*, 1989, **61**, 1681; 1990, **62**, 1155; J. T. B. H. Jastrzebski and G. van Koten, *Adv. Organomet. Chem.*, 1993, **35**, 241.

3 L. Contreras, A. H. Cowley, F. P. Gabbai, R. A. Jones, C. J. Carrano and M. R. Bond, *J. Organomet. Chem.*, 1995, **489**, C1.

4 H. Schumann, U. Hartmann and W. Wassermann, *Chem. Ber.*, 1991, **124**, 1567.

5 H. Schumann, W. Wassermann and A. Dietrich, *J. Organomet. Chem.*, 1989, **365**, 11.

6 M. Lauer and G. Wulff, *J. Organomet. Chem.*, 1983, **256**, 1.

7 S. Toyota, T. Futawaka, H. Ikeda and M. Oki, *J. Chem. Soc., Chem. Commun.*, 1995, 2499.

8 M. Lauer, H. Böhnke, R. Grotstollen, M. Salehnia and G. Wulff, *Chem. Ber.*, 1985, **118**, 246.

9 The only known examples of transition-metal boranediyl complexes are $[(CO)_4FeB(NMe_2)]$ (G. Schmid, W. Petz and H. Nöth, *Inorg. Chim. Acta*, 1970, **4**, 423) and $[\{(C_5H_4R)(CO)_2Mn\}_2(\mu\text{-}BX)]$, with X = NMe_2, R = H, Me; X = Bu^t, R = Me (H. Braunschweiger and T. Wagner, *Angew. Chem.*, 1995, **107**, 904).

10 W. N. Setzer and P. v. Rague-Schleyer, *Adv. Organomet. Chem.*, 1985, **24**, 353 and references therein.

11 P. v. Rague-Schleyer, R. Hacker, H. Dietrich and W. Mahdi, *J. Chem. Soc., Chem. Commun.*, 1985, 662.

12 S. Harder, J. Boersma, L. Brandsma, J. A. Kanters, W. Bauer and P. v. Rague-Schleyer, *Organometallics*, 1989, **8**, 1696; D. Thoennes and E. Weiss, *Chem. Ber.*, 1978, **111**, 3157; J. T. B. H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen and M. Pfeffer, *J. Organomet. Chem.*, 1983, **246**, C75; M. A. Beno, H. Hope, M. M. Olmstead and P. P. Power, *Organometallics*, 1985, **4**, 2117.

13 A. A. H. van der Zeijden and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 431.

14 J. T. B. H. Jastrzebski, G. van Koten, M. Konijn and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 5490.

15 M. Hesse, H. Meier and B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, Georg-Thieme-Verlag, Stuttgart–New York, 4th edn., 1991.

16 H. Hess, *Acta Crystallogr., Sect. B*, 1969, **25**, 2338.

17 B. P. Buffin, M. J. Poss, A. M. Arif and T. G. Richmond, *Inorg. Chem.*, 1993, **32**, 3805.

18 SHELXTL PLUS, Siemens Analytical X-ray Instruments Inc., 1990, XS: Program for Crystal Structure Solution, XL: Program for Crystal Structure Determination, XP: Interactive Molecular Graphics.

Received, 30th September 1996; Com. 6/06670D