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Preliminary Communication

A novel aryllithium · lithium bromide complex containing an anionic pentadentate organylpolyamine system enfolding two lithium centres

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Abstract

The aryllithium compound $\text{Li}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-2,6]\text{Br}$, which has been characterized by an X-ray crystallographic determination and by NMR spectroscopy, was obtained from the reaction of $[\text{C}_6\text{H}_3\text{Br}(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-2,6]$ with 2 equivalents of ${}^n\text{BuLi}$. The lithium compound has a novel structural feature: a Li_2ArBr core in which the bromide is bridge-bonded (LiBrLi' 64.8(2)°) and C_{ipso} is involved in a three-centre two electron (3c-2e) bond (LiCLi' 72.2(2)°). The coordination sphere of each lithium atom is completed by coordination with the two N-donor atoms of the *ortho*- $\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ substituents.

There is continuing interest in the theoretical and mechanistic aspects of $\text{C}_{ipso}\text{-Li}$ bonding in aryllithium compounds [1]. Several synthetic, structural and theoretical studies of aryllithium complexes containing the N,C,N terdentate ligand system $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6]^-$ and the related C,N,N' terdentate ligand $[\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2-2]^-$ (see Fig. 1) have been carried out, not least because these aryllithium compounds are important and often crucial reagents for the introduction of these ligands into organometallic species [2] with diverse features [3]. The C,N,N' ligand is particularly interesting in that it can be regarded as a derivative of tmeda (tetramethylethylenediamine) in which a methyl group has been replaced by a benzyl group that provides additional C-coordinating potential at one *ortho* aryl position. A characteristic

feature of both solution and solid state structures of the N,C,N and C,N,N' lithium compounds is the three-centre two-electron bond of the $\text{Li-C-Li}'$ unit [1b,3b].

We now have designed and synthesized a new pentadentate ligand $[\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-2,6]^-$ having an aryl skeleton with two $-\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ substituents *ortho* to an anionic C_{ipso} site. Because this ligand is a potentially N',N,C,N,N' binding system it is possible that when it is C-bonded to a metal centre the four N-donor sites may further encapsulate the metal to form a small organometallic cavity. We report below the synthesis and structural characterization of the lithium derivative of this ligand – an aryllithium compound that gains stability by binding one equivalent of lithium bromide.

The 1:2 molar reaction of the aryl bromide $[\text{C}_6\text{H}_3\text{Br}(\text{CH}_2\text{Br})_2-2,6]$ with $\text{HN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ in the presence of NEt_3 as a base affords the bis *ortho*-diamine-substituted aryl bromide $[\text{C}_6\text{H}_3\text{Br}(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-2,6]$ (1) (see Scheme 1) which was characterized by ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectroscopy [4*]. Treatment of 1 with two equivalents of ${}^n\text{BuLi}$ results in Li/Br exchange to give the air- and moisture-sensitive white crystalline compound 2, of formula $\text{Li}_2[\text{C}_6\text{H}_3\text{-(CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-2,6]\text{Br}$, in 75% yield (see Scheme 1). (Quenching of a solution of 2 in toluene- d_6 with an excess of D_2O resulted in quantitative formation of $[\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-1,3\text{-D-2}]$, which proved that complete lithiation took place at one position of the aryl ring [5*].)

From the ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of 2 [6*] a number of structural conclusions can be drawn: (i) there is only one resonance pattern observed for the *ortho* substituents, and therefore there is a C_2 axis in 2 running through C_{ipso} and C_{para} , and (ii) there is only one sharp lowfield-shifted resonance for the $-\text{N}(\text{Me})-$ protons, which means not only that $\text{Li-N}(\text{Me})$ coordination is rigid on the NMR time scale but also that

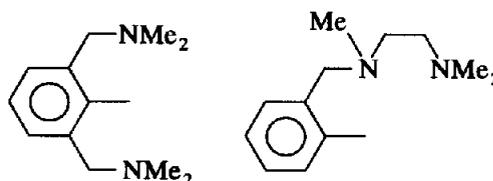
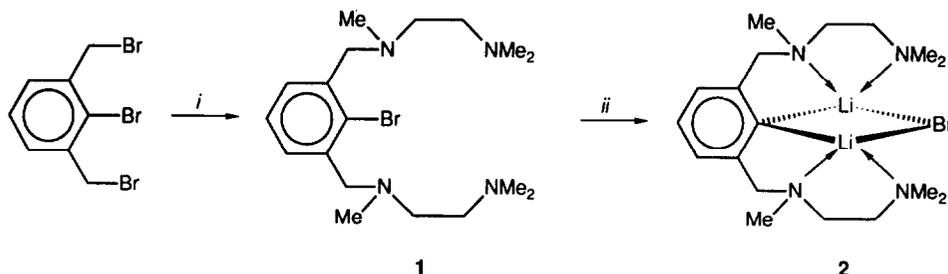


Fig. 1. The terdentate ligand systems N,C,N and C,N,N'.

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Scheme 1. Reagents and conditions: (i) 2 equivalents of HN(Me)CH₂CH₂NMe₂, excess of NEt₃, benzene, RT, 2 h; (ii) 2 equivalents of ⁿBuLi, diethyl ether, -70°C, 2 h.

both of these stereogenic -N(Me)- centres have the same configuration. To aid our interpretation of these data the solid state structure of 2 was elucidated by an X-ray crystallographic study carried out on a crystal obtained from a cooled diethyl ether solution. The unit cell contains two enantiomeric molecules of 2. The enantiomers are the *S_NS_N* and *R_NR_N* complexes, arising from the presence of two stereogenic -N(Me)-centres in each complex. Figure 2 shows the molecular structure of one of these enantiomers [7*], *i.e.* the *S_NS_N* one, together with the adopted numbering scheme.

The molecular geometry of 2 shows it to be a [Li₂(Ar)Br] complex in which two Li atoms are bridged by C_{ipso} (= C(1)) of a single arylamine ligand and a Br atom, which together provide the planar Li₂C_{ipso}Br core. Each *ortho*-CH₂N(Me)CH₂CH₂NMe₂ substituent binds through its two N-atoms to complete the coordination sphere of a lithium atom.

The Li(1)-C(1)-Li(2) angle is acute (72.7(2)°), indicating that C_{ipso} is involved with the lithium centres in a three-centre, two electron (3c-2e) bond. This structure can be compared with that of the phenyllithium cluster [(LiPh · OEt₂)₃ · LiBr] in which the C_{ipso} and Br atoms are involved in (4c-2e) bonds [8]. The Li(1)-Br-Li(2) angle is also acute (64.8(2)°), and as discussed extensively for many common M-Br-M' bridges this is also best interpreted in terms of a three-centre, two-electron bond. The Li-Br distances are 2.455(5) and 2.468(6) Å, with a Li ··· Li separation of 2.637(8) Å; by comparison, in Li₂[C₆H(CH₂NMe₂)_{4-2,3,5,6}]₂, in which the two Li centres are bridged by two C_{ipso} centres, the Li ··· Li separation is 2.401(6) Å [1i].

The aryl ring shows considerable distortion, with a reduced C(2)-C(1)-C(6) angle (115.1(3)°) and lengthened C(1)-C(2) and C(1)-C(6) bonds (1.403(5) and

1.413(5) Å, respectively). This small angle appears to be normal for aryl metal complexes in which a C_{ipso} atom bridges an electropositive metal; for example, it is 113.7° in (Ph₃Al)₂ and 111.8(3)° in [Li₂Ph₂(tmeda)₂] [1i,9,10]. The angle between the Li(1)-C(1)-Li(2)-Br plane and the aryl plane is 58.0(2)° and, although a 3c-2e bonding mode commonly leads to a perpendicular orientation between the aryl plane and the coordination plane in organolithium species [8,9,11], this angle is similar to that found in organolithium compounds containing intramolecularly-coordinating ligands that result in involvement of C_{ipso} in five-membered chelate rings [1c,i]. Compound 2 can be regarded as an aryldilithio bromide in which the donor atom arrangement of the new pentadentate ligand creates an [ArLi₂]⁺ cation to which a bromide anion is bridge-bonded. The mechanism of the Li/Br exchange reaction of BuLi with the aryl bromide 1 that leads to 2 is

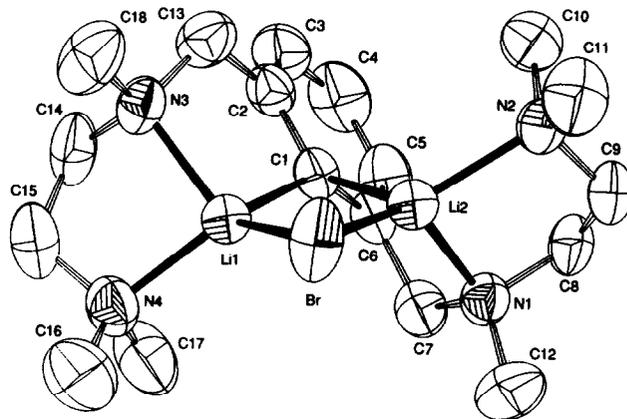


Fig. 2. Thermal motion ellipsoid plot (drawn at 50% probability level) of Li₂[C₆H₃(CH₂N(Me)CH₂CH₂NMe₂)_{2,2,6}]Br (2) together with the adopted numbering scheme. Selected bond distances (Å) and angles (°): Li(1)-C(1) 2.196(6), Li(1)-Br 2.455(5), Li(1)-N(3) 2.056(7), Li(1)-N(4) 2.100(7), Li(2)-C(1) 2.252(7), Li(2)-Br 2.468(6), Li(2)-N(1) 2.097(7), Li(2)-N(2) 2.120(7), Li ··· Li 2.637(8); Li(1)-C(1)-Li(2) 72.7(2), Li(1)-Br-Li(2) 64.8(2), C(2)-C(1)-C(6) 115.1(3).

* Reference number with asterisk indicates a note in the list of references.

currently being examined, and preliminary results give support to the proposal by Reich *et al.* that such exchange reactions may involve ionic ate species $[\text{Ar}-\text{Br}-\text{Bu}]^-\text{Li}^+$ [1j]. An interesting property of this new monoanionic pentadentate $\text{N}'\text{,N,C,N,N}'$ ligand system is its clear potential for binding two metal atoms in the same small organic cavity within a short distance of each other: this aspect is now finding application in our research programme on the synthesis of interesting homo- and hetero-binuclear organometallic species [12*].

Acknowledgements

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- 1: ^1H NMR (200.13 MHz, C_6D_6 , 298 K) δ 7.53 (d, 2H, ArH, $^3J(\text{HH})$ 7 Hz), 7.13 (t, 1H, ArH, $^3J(\text{HH})$ 7 Hz), 3.48 (s, 4H, ArCH_2N), 2.53 (m, 4H, $-\text{CH}_2-$), 2.40 (m, 4H, $-\text{CH}_2-$), 2.18 (s, 6H, NCH_3), 2.10 (s, 12H, $\text{N}(\text{CH}_3)_2$), ^{13}C NMR (50 MHz, C_6D_6 , 298 K) δ 139.7 ($2 \times \text{ArC}$), 129.3 (ArC), 128.5 ($2 \times \text{ArC}$), 127.0 (C_{ipso}), 62.8 (ArCH_2N), 58.2 ($-\text{CH}_2-$), 56.4 ($-\text{CH}_2-$), 45.9 ($\text{N}(\text{CH}_3)_2$), 42.8 (NCH_3).
- 5 $[\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2)_2-1,3\text{-D-2}]$: ^1H NMR (200.13 MHz, toluene- d_8 , 298 K) δ 7.3–7.15 (m, 3H, ArH), 3.41 (s, 4H, ArCH_2N), 2.45 (m, 4H, $-\text{CH}_2-$), 2.35 (m, 4H, $-\text{CH}_2-$), 2.12 (s, 6H, NCH_3), 2.09 (s, 12H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (50 MHz, toluene- d_8 , 298 K) δ 140.0 ($2 \times \text{ArC}$), 129.2 (C(2), $^1J(\text{CD})$ 24 Hz), 128.3 (ArC), 127.8 ($2 \times \text{ArC}$), 63.2 (ArCH_2N), 58.3 ($-\text{CH}_2-$), 56.1 ($-\text{CH}_2-$), 45.9 ($\text{N}(\text{CH}_3)_2$), 42.7 (NCH_3).
- 2: ^1H NMR (200.13 MHz, toluene- d_8 , 298 K) δ 7.08 (t, 1H, ArH, $^3J(\text{HH})$ 7 Hz), 6.89 (d, 2H, ArH, $^3J(\text{HH})$ 7 Hz), 3.92 (d, 2H, ArCH_2N , $^2J(\text{HH})$ 12 Hz), 3.12 (d, 2H, ArCH_2N , $^2J(\text{HH})$ 12 Hz), 2.54 (td, 2H, $-\text{CH}_2-$, $^2J(\text{HH})$ 12 Hz, $^3J(\text{HH})$ 3 Hz), 2.37 (s, 6H, NCH_3), 2.11 (td, 2H, $-\text{CH}_2-$, $^2J(\text{HH})$ 12 Hz, $^3J(\text{HH})$ 3 Hz), \sim 2.1 (br s, 6H, $-\text{N}(\text{CH}_3)_2$), 1.57 (dt, 2H, $-\text{CH}_2-$, $^2J(\text{HH})$ 12 Hz, $^3J(\text{HH})$ 3 Hz), \sim 1.4 (br s, 6H, $-\text{N}(\text{CH}_3)_2$), 1.39 (dt, 2H, $-\text{CH}_2-$, $^3J(\text{HH})$ 12 Hz, $^3J(\text{HH})$ 3 Hz). ^{13}C NMR (50 MHz, toluene- d_8 , 298 K) δ 151.5 ($2 \times \text{ArC}$), 124.7 (ArC), 124.3 ($2 \times \text{ArC}$), 70.4 (ArCH_2N), 57.6 ($-\text{CH}_2-$), 52.0 ($-\text{CH}_2-$), \sim 52 (br, $\text{N}(\text{CH}_3)_2$), \sim 47 (br, $\text{N}(\text{CH}_3)_2$), 43.9 (NCH_3). C_{ipso} not observed.
- 7 Crystal data for 2: $\text{C}_{18}\text{H}_{33}\text{BrLi}_2\text{N}_4$, $M = 399.27$, yellow crystal in capillary, triclinic; space group $P\bar{1}$, $a = 8.266(2)$, $b = 11.552(1)$, $c = 12.280(1)$ Å, $\alpha = 81.07(1)^\circ$, $\beta = 86.69(1)^\circ$, $\gamma = 74.82(1)^\circ$, $U = 1117.8(3)$ Å³, $D_c = 1.186$ g cm⁻³, $Z = 2$, $F(000) = 420$, $\text{Mo K}\alpha$ (monochromated) radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo K}\alpha) = 18.2$ cm⁻¹. Intensities for 8067 reflections were collected at 295 K [CAD-4T/rotating anode; $\theta_{\text{max}} = 27.5^\circ$; $\omega/2\theta$ -scan] and averaged ($R_{\text{int}} = 0.068$) into 3039 unique reflections with $I > 2.5\sigma(I)$. The structure was solved by Direct Methods (SHELXS-86) and refined by full-matrix least-squares techniques (SHELXL76) to $R = 0.049$ [$wR = 0.044$, $w = 1/\sigma^2(F)$, $S = 0.72$; $-0.77 < \Delta\rho < 0.84$ e Å⁻³]. Hydrogen atoms were accounted for at calculated positions. Atomic coordinates, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.
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- 12 Recent examples are $\text{TaCl}_2\{\mu\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\mu\text{-C}^t\text{Bu})$ (ZnCl) (H. C. L. Abbenhuis, N. Feiken, H. F. Haarman, D. M. Grove, E. Horn, H. Kooijman, A. L. Spek and G. van Koten, *Angew. Chem., Int. Ed. Engl.*, **30** (1991) 996) and $\text{Cu}_5\text{Br}_3\text{-}[\text{C}_6\text{H}_3(\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{Me}_2)_2\text{-2,6}]_2$ which consists of two $[\text{Cu}_2(\text{Ar})]^+$ cationic units bridged by a CuBr_3^{2-} dianion (G. M. Kapteijn, I. C. M. Wehman-Ooyevaar, W. J. J. Smeets, A. L. Spek and G. van Koten, *Angew. Chem., Int. Ed. Engl.*, **32** (1992) 72).