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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 $Li_2[C_6H_3\{CH_2N(Me)CH_2CH_2NMe_2\}_2$-2,6]Br, which has been characterized by an X-ray crystallographic determination and by NMR spectroscopy, was obtained from the reaction of $[C_6H_3Br\{CH_2N(Me)CH_2CH_2NMe_2\}_2$-2,6] with 2 equivalents of ^nBuLi. 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*-$CH_2N(Me)CH_2CH_2NMe_2$ substituents.

There is continuing interest in the theoretical and mechanistic aspects of C_{ipso}–Li bonding in aryllithium compounds [1]. Several synthetic, structural and theoretical studies of aryllithium complexes containing the N,C,N terdentate ligand system $[C_6H_3\{CH_2NMe_2\}_2$-2,6]$^-$ and the related C,N,N′ terdentate ligand $[C_6H_4CH_2N(Me)CH_2CH_2NMe_2$-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in that it can be regarded as a derivative of tmeda (tetramethylethylenediamine) in which a methyl group has been replaced by a benzyl group that provides additional C-coordinating potential at one *ortho* aryl position.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 Li–C–Li′ unit [1b,3b].

We now have designed and synthesized a new pentadentate ligand $[C_6H_3\{CH_2N(Me)CH_2CH_2NMe_2\}_2$-2,6]$^-$ having an aryl skeleton with two $-CH_2N(Me)CH_2CH_2NMe_2$ 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 $[C_6H_3Br\{CH_2Br\}_2$-2,6] with $HN(Me)CH_2CH_2NMe_2$ in the presence of NEt_3 as a base affords the bis *ortho*-diamine-substituted aryl bromide $[C_6H_3Br\{CH_2N(Me)CH_2CH_2NMe_2\}_2$-2,6] (**1**) (see Scheme 1) which was characterized by ^1H and ^{13}C NMR spectroscopy [4*]. Treatment of **1** with two equivalents of ^nBuLi results in Li/Br exchange to give the air- and moisture-sensitive white crystalline compound **2**, of formula $Li_2[C_6H_3\{CH_2N(Me)CH_2CH_2NMe_2\}_2$-2,6]Br, in 75% yield (see Scheme 1). (Quenching of a solution of **2** in toluene-d_8 with an excess of D_2O resulted in quantitative formation of $[C_6H_3\{CH_2N(Me)CH_2CH_2NMe_2\}_2$-1,3-D-2], which proved that complete lithiation took place at one position of the aryl ring [5*].)

From the ^1H and ^{13}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 –N(Me)– protons, which means not only that Li–N(Me) coordination is rigid on the NMR time scale but also that

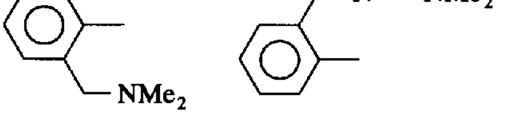

Fig. 1. The terdentate ligand systems N,C,N and C,N,N′.

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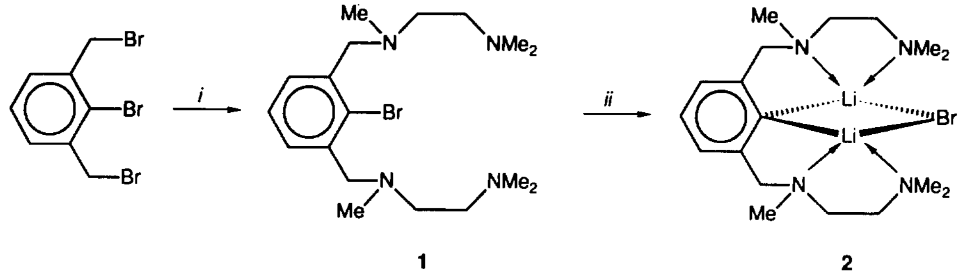

Scheme 1. *Reagents and conditions*: (i) 2 equivalents of $HN(Me)CH_2CH_2NMe_2$, excess of NEt_3, benzene, RT, 2 h; (ii) 2 equivalents of ^nBuLi, diethyl ether, −70°C, 2 h.

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 $[Li_2(Ar)Br]$ 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 $Li_2C_{ipso}Br$ core. Each *ortho*-$CH_2N(Me)CH_2CH_2NMe_2$ 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 $[(LiPh \cdot OEt_2)_3 \cdot LiBr]$ 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 $Li_2[C_6H(CH_2NMe_2)_4\text{-}2,3,5,6]_2$, 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 $(Ph_3Al)_2$ and 111.8(3)° in $[Li_2Ph_2(tmeda)_2]$ [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 $[ArLi_2]^+$ 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

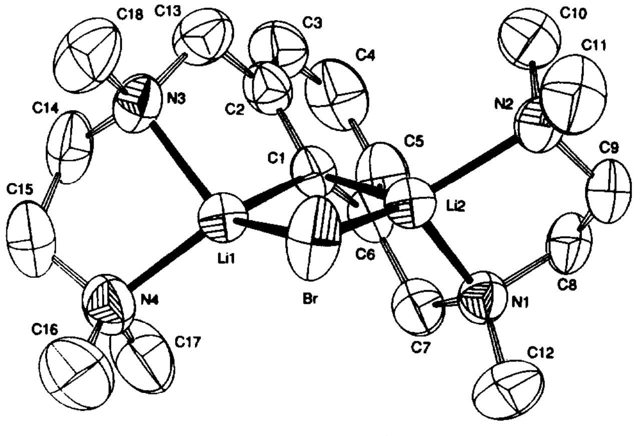

Fig. 2. Thermal motion ellipsoid plot (drawn at 50% probability level) of $Li_2[C_6H_3\{CH_2N(Me)CH_2CH_2NMe_2\}_2\text{-}2,6]Br$ (**2**) together with the adopted numbering scheme. Selected bond distances (Å) and angles (°): Li(1)–C(1) 2.196(6), Li(1)–Br 2.455(5), Li(1)–N(3) 2.056(7), Li(1)–N(4) 2.100(7), 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).

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* 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 $[\text{Ar–Br–Bu}]^-\text{Li}^+$ [1j]. An interesting property of this new monoanionic pentadentate N′,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*].

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4 **1**: ^{1}H NMR (200.13 MHz, C_6D_6, 298 K) δ 7.53 (d, 2H, ArH, ^3J(HH) 7 Hz), 7.13 (t, 1H, ArH, ^3J(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, $\text{N(CH}_3)_2$), ^{13}C NMR (50 MHz, C_6D_6, 298 K) δ 139.7 (2×ArC), 129.3 (ArC), 128.5 (2×ArC), 127.0 (C_{ipso}), 62.8 (ArCH_2N), 58.2 ($-\text{CH}_2-$), 56.4 ($-\text{CH}_2-$), 45.9 ($\text{N(CH}_3)_2$), 42.8 (NCH_3).

5 $[\text{C}_6\text{H}_3\{\text{CH}_2\text{N(Me)CH}_2\text{CH}_2\text{NMe}_2\}_2\text{-1,3-D-2}]$: ^{1}H 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, $\text{N(CH}_3)_2$). ^{13}C NMR (50 MHz, toluene-d_8, 298 K) δ 140.0 (2×ArC), 129.2 (C(2), ^1J(CD) 24 Hz), 128.3 (ArC), 127.8 (2×ArC), 63.2 (ArCH_2N), 58.3 ($-\text{CH}_2-$), 56.1 ($-\text{CH}_2-$), 45.9 ($\text{N(CH}_3)_2$), 42.7 (NCH_3).

6 **2**: ^{1}H NMR (200.13 MHz, toluene-d_8, 298 K) δ 7.08 (t, 1H, ArH, ^3J(HH) 7 Hz), 6.89 (d, 2H, ArH, ^3J(HH) 7 Hz), 3.92 (d, 2H, ArCH_2N, ^2J(HH) 12 H), 3.12 (d, 2H, ArCH_2N, ^2J(HH) 12 Hz), 2.54 (td, 2H, $-\text{CH}_2-$, ^2J(HH) 12 Hz, ^3J(HH) 3 Hz), 2.37 (s, 6H, NCH_3), 2.11 (td, 2H, $-\text{CH}_2-$, ^2J(HH) 12 Hz, ^3J(HH) 3 Hz), ~ 2.1 (br s, 6H, $-\text{N(CH}_3)_2$), 1.57 (dt, 2H, $-\text{CH}_2-$, ^2J(HH) 12 Hz, ^3J(HH) 3 Hz), ~ 1.4 (br s, 6H, $-\text{N(CH}_3)_2$), 1.39 (dt, 2H, $-\text{CH}_2-$, ^3J(HH) 12 Hz, ^3J(HH) 3 Hz). ^{13}C NMR (50 MHz, toluene-d_8, 298 K) δ 151.5 (2×ArC), 124.7 (ArC), 124.3 (2×ArC), 70.4 (ArCH_2N), 57.6 ($-\text{CH}_2-$), 52.0 ($-\text{CH}_2-$), ~ 52 (br, $\text{N(CH}_3)_2$), ~ 47 (br, $\text{N(CH}_3)_2$), 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, $\alpha = 81.07(1)°$, $\beta = 86.69(1)°$, $\gamma = 74.82(1)°$, $U = 1117.8(3)$ Å^3, $D_c = 1.186$ g cm^{-3}, $Z = 2$, $F(000) = 420$, Mo Kα (monochromated) radiation ($\lambda = 0.71073$ Å), μ(Mo Kα) = 18.2 cm^{-1}. Intensities for 8067 reflections were collected at 295 K [CAD-4T/rotating anode; $\theta_{max} = 27.5°$; $\omega/2\theta$-scan] and averaged ($R_{int} = 0.068$) 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 (SHELX76) 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 $\text{TaCl}_2\{\mu\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\mu\text{-C-}^t\text{Bu})(\text{ZnCl})$ (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 $\text{Cu}_5\text{Br}_3[\text{C}_6\text{H}_3\{\text{CH}_2\text{N(Me)CH}_2\text{CH}_2\text{Me}_2\}_2\text{-2,6}]_2$ 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).