The First Structurally Characterised Early Main-group Metal Diazaallyl Complex; Synthesis and Crystal Structure of $LiCPh(NPh)_2{\cdot}NMe[(CH_2)_2NMe_2]_2$

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n-Butyllithium reacts with a solution of PhNC(Ph)NHPh (*N,N'*-diphenylbenzamidine) and $NMe[(CH_2)_2NMe_2]_2$ (pmdeta) to give the complex $LiCPh(NPh)_2{\cdot}$pmdeta, which is monomeric in the solid state with a five-co-ordinate lithium cation bound to a tridentate pmdeta ligand and a bidentate amidinide anion (diazaallyl system, chelating), in which the two N–C bond lengths of 1.336(4) and 1.335(4) Å suggest almost uniform delocalisation along the $N{\cdots}C{\cdots}N$ unit.

Early main-group metallation of multifunctional organic acids has been intensively investigated by ourselves [1] and by others [2] in recent years. The redistribution of electron density within an organic ligand caused by the introduction of a highly electropositive metal is a point of particular interest. Alteration of relative bond lengths within,[1a,2a] and even major rearrangement of,[1b,1c,2b] the covalent framework of the formally anionic ligand has been seen in previous cases. In an extension of this work to the lithiation of a benzamidine, we here report the synthesis and low-temperature X-ray crystal structure determination of the lithioamidinide complex $LiCPh(NPh)_2{\cdot}$pmdeta **1** (pmdeta = *N,N,N',N'',N''*-pentamethyldiethylenetriamine).

Complex **1** was prepared by lithiating a solution of *N,N'*-diphenylbenzamidine in toluene–tetrahydrofuran (thf) in the presence of pmdeta.† Pale yellow crystals of **1** were isolated after 2 d at −20 °C and characterised by X-ray diffraction ‡ and spectroscopic techniques.† The solid-state structure (Fig. 1) shows **1** to be monomeric with a five-co-ordinate lithium cation chelated by the bidentate amidinide anion and by a tridentate pmdeta donor ligand. The core unit is a $\overline{\text{NCNLi}}$ four-membered ring which forms a non-crystallographic plane. Within the amidinide unit, **1** exhibits essentially uniform C–N distances [N(2)–C(19) 1.336(4), N(1)–C(19) 1.335(4) Å] which are almost an exact average of the C=N [1.302(7) Å] and C–N [1.360(8) Å] bond lengths in the protonated, uncomplexed ligand,[5] suggesting uniform delocalisation throughout the three-atom central unit. It thus appears that the anion in **1** might best be described as a diazaallyl system. This description of the ligand is supported by the near planarity of the C(13)–N(2)–C(19)–N(1)–C(7) unit {X–N(2)–C(13) 163.0, X–N(1)–C(7) 157.2° [X = centroid of LiN(1)C(19)N(2) plane]}. The slight deviation from the plane can be explained by the electrostatic repulsion between the nitrogen [N(1),N(2)] sp^2 lone pairs. This effect is itself countered by the electrostatic attraction of the lithium cation for each nitrogen lone pair pulling the C(13)–N(2)–C(19)–N(1)–C(7) unit towards planarity. The two distinct anion–lithium bond lengths [N(2)–Li 2.188(6) Å; N(1)–Li 2.076(6) Å] are generated by the position of the pmdeta ligand; on the N(2) side of the molecule there are two Li–N interactions with the donor pmdeta molecule [Li–N(3) and Li–N(5)] compared to only one [Li–N(4)] interaction on the N(1) side. Hence to gain an even charge distribution around the lithium cation the Li–N(2) interaction is elongated relative to the Li–N(1) interaction (av. 2.132 Å).

Several transition-metal complexes containing the *N,N'*-diphenylbenzamidinide ligand have been reported, with the ligand exhibiting either a bidentate chelating mode[6,7] or a monodentate bridging mode,[8,9] and even both modes in the same molecule.[10] In some of these examples the lithiated amidine has been used as a precursor during the preparation of the transition-metal complex.[6,10–12] The preparation has involved lithiating a chilled ether solution of the amidine to give a suspension of the lithioamidinide which is then either used immediately or stored frozen. Previous investigations involving ^{13}C and ^{7}Li NMR spectroscopy have been performed on lithiated amidines with and without complexation by hexamethylphosphoramide (hmpa), and a preliminary, partially solved room-temperature crystal structure of $[Li\{CMe(NPh)_2\}{\cdot}$

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† Experimental data for **1**: To a solution of *N,N'*-diphenylbenzamidine (Aldrich) (5 mmol, 1.36 g) and pmdeta (5 mmol, 1.05 cm^3) in toluene (4 cm^3)–thf (3 cm^3) (chilled in a liquid-N_2 bath) was added *n*-butyllithium (5 mmol of a 1.6 mol dm^{-3} solution in hexane). The solution was allowed to warm to room temperature with constant stirring. Gentle heating gave a clear dark orange solution from which half the solvent was removed *in vacuo*, followed by layering with hexane (2 cm^3). Refrigeration at −20 °C for 2 d yielded pale yellow, air-sensitive crystals of **1** (1.25 g, 55%, m.p. 151–153 °C, satisfactory C, H and N analyses for $C_{28}H_{38}LiN_5$ were obtained). ^1H NMR (250 MHz, $[^2H_8]$thf, 293 K): δ 8.5–6.5 (series of broad unresolved s, 15 H, PhNCPhNPh), 2.5–2.3 (m, 8 H), 2.33 (s, 3 H), 2.16 (s, 12 H) (all pmdeta, 23 H).

‡ Crystal data for $LiCPh(NPh)_2{\cdot}NMe[(CH_2)_2NMe_2]_2$ **1**: $C_{28}H_{38}LiN_5$, $M = 451.57$, monoclinic, space group $P2_1/c$, $a = 11.873(2)$, $b = 18.103(4)$, $c = 12.774(3)$ Å, $\beta = 90.08(3)°$, $U = 2745.6(10)$ Å^3, $F(000) = 976$, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 0.065 mm^{-1}, $T = 153(2)$ K, $Z = 4$, $D_c = 1.092$ Mg m^{-3}, dimensions 0.25 × 0.25 × 0.25 mm. Data were collected on a Stoe-Siemens diffractometer in the range $5 \leqslant 2\theta \leqslant 45°$ (6059 reflections collected, 3579 independent reflections). The structure was solved by direct methods[3] and refinement, based on F^2, was by full-matrix least-squares techniques[4] (all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions) to $R_1 = 0.0649$, $wR_2 = 0.1934$ $\{w = 1/[\sigma^2F_o^2 + (0.1802P)^2 + 1.04P]$, where $P = (0$ or $F_o^2 + 2F_c^2)/3\}$ for 2997 unique reflections $[I > 2\sigma(I)]$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

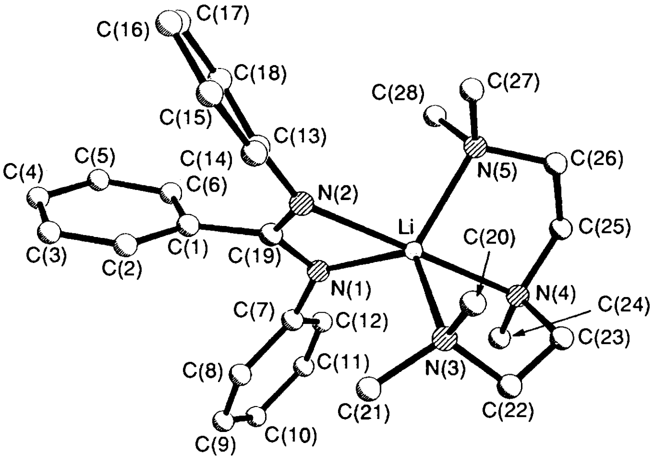

Fig. 1 Molecular structure of LiCPh(NPh)$_2$·pmdeta **1** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Li–N(1) 2.076(6), Li–N(2) 2.188(6), Li–C(19) 2.504(6), Li–N(3) 2.162(6), Li–N(4) 2.235(6), Li–N(5) 2.139(6), N(1)–C(19) 1.335(4), N(2)–C(19) 1.336(4), N(1)–Li–N(2) 64.4(2), N(1)–C(19)–N(2) 116.7(3), C(7)–N(1)–C(19) 121.4(3), C(13)–N(2)–C(19) 121.6(3)

hmpa]$_2$ has been obtained.[13,14] However, **1** is the first accurate crystal structure of an early main-group metal cation chelated by a diazaallyl unit, allowing comparison with the structures of known azaallyl lithium[15] and sodium[16] complexes. In addition, a number of complexes have been structurally characterised which possess a $[RN(C_5H_4N)]^-$ (R = Me_3Si[17] or Ph[18,19]) anion chelating a lithium cation, but these are not strictly amidines and do not possess the fully delocalised diazaallyl N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N unit found in **1**.

A comparison of **1** with transition-metal complexes of the ligand reveals a significant difference between the N(1)–C(19)–N(2) angle in **1** [116.74(27)°] and in platinum [106.7(5)°][6] and rhodium [110.0(6)°][7] complexes of the ligand. This can be explained in terms of the more ionic bonding of **1** being less directionally constrained than the more covalent bonding within the transition-metal complexes. Additionally the tridentate pmdeta chelating the lithium cation will increase the amidinide 'bite' angle by repulsive steric interactions with the substituent phenyl groups on the N$\overset{\cdots}{-}$C$\overset{\cdots}{-}$N unit. The small ionic radius of Li^+ will accentuate this steric effect, especially in the five-co-ordinate system observed in **1**.

Comparison of the planar $\overline{\text{N(1)C(19)N(2)Li}}$ core of **1** to similar four-membered cores in early main-group azaallyl complexes,[15,16] and in polymeric benzyllithium,[20] clearly shows the change in bonding mode (from η^3 to σ,σ) of the lithium cation to the various allyl type anions. In benzyllithium[20] the lithium cation sits asymmetrically above the allyl plane and is located closest to the benzylic carbon. Carbon-13 NMR studies[21] confirm allyllithium as an asymmetric π structure. For the lithium η^3-azaallyl complexes[15] the LiNCC core unit is again non-planar and asymmetrically distorted towards the nitrogen; similarly the Na sits over the N, above the CNC plane in the NaCNC core of the sodium azaallyl system.[16] For **1**, however, the core unit is planar. This planarity confirms that it is the sp^2 lone pair on each nitrogen [N(1), N(2)] which is involved in bonding to the lithium cation, rather than any electrostatic interaction with the delocalised allyl π system, which would require positioning of the lithium cation above the NCN plane.

The room-temperature ^{1}H NMR spectrum of **1** shows broad unresolved signals in the aromatic region, consistent with *syn–anti* flipping of the phenyl groups attached to each N of the NCN unit. Such rotation of the partially doubly bonded N$\overset{\cdots}{-}$C linkage might be expected to be slow at room temperature; however variable-temperature multinuclear and multidimensional NMR are required to investigate this process fully.

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