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Bulky formamidinate complexes of lithium: the first examples of η^2:η^1-C=N,N′ metal amidinate coordination

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The lithium complexes [Li{N(Ar)C(H)N(Ar)}(pmdeta)], where Ar = 2,6-$R_2C_6H_3$ (R = Me (1), Et (2) and ^{i}Pr (3)) and pmdeta = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, have been synthesised and their solid state structures determined by X-ray methods. Compounds 1–3 comprise a Li(pmdeta) centre coordinated by a bulky formamidinate in either the *E-syn* or *E-anti* isomeric form. The structures of compound 3 and one unique molecular unit of compound 1 (*E-anti* isomer) display coordination of the *pendant* amidinate imine, and can therefore be considered the first examples of η^2:η^1-C=N,N′ metal amidinate coordination.

Introduction

Over the past three decades, the amidinate ($[R^1NC(R^2)NR^3]^-$) family of ligands has come to the fore in organoamido chemistry[1] as cyclopentadienyl ('Cp') replacements in transition metal chemistry, support ligands in catalysis, and scaffolds for bimetallic paddlewheel complexes with varying orders of M–M bonding. This considerable interest has generated a significant number of structurally-characterised metal amidinate complexes.[2] It could be expected, therefore, that the easily derivatised anionic 1,3-diazaallyl donor set of amidinates would have led to several well-established coordination modes; however, this is not the case. Based on currently available data, metal amidinate coordination modes can be separated into three classes that each rely on two or four electron nitrogen σ-donation (see Fig. 1): monodentate **A**,[3] bidentate chelating **B**[4] and bimetallic bridging **C**.[5] Of these, **B** and **C** are the more common modes, **B** being the expected coordination when **C** is not sterically or electronically favoured, while examples of **A** are relatively scarce.[6]

In principle, several variations of coordination class **B** are also possible. These binding subclasses arise from variations in electron localisation within the anionic NCN backbone of the amidinate. For instance, the nitrogen donors of a symmetrically substituted charge delocalised amidinate can interact equally with the chelated metal centre to give M–N bond lengths and amidinate backbone C–N bond lengths representative of a conjugated donor (**B**). This occurs for the compound $[Al(CH_3)_2\{N(c\text{-}C_6H_{11})C(CH_3)N(c\text{-}C_6H_{11})\}]$ (1.923(2)/1.926(2) and 1.329(3)/1.325(2) Å, respectively).[7] However, if charge localisation at one nitrogen is favoured, discrete C–N and C=N bonds can result across the amidinate. In this instance, two types of four electron donation are possible (see **D** and **E**, Fig. 1), aside from monodentate coordination type **A**.[3] The first, **D**, requires imine N-electron pair donation. Unlike **B**, this bonding mode is accompanied by distinct differences in M–N and backbone C–N bond lengths that represent a move towards discrete metal–amide and metal–imine bonds, respectively. The compound $[Ti\{N(^iPr)C(NMe_2)N(^iPr)\}_2\{C(NC_6F_5)(N^iPr)\text{=}N(^iPr)\}]$ contains an amidinate that exemplifies type **D** coordination (Ti–N_{amido} = 2.061(3), Ti–N_{imino} = 2.127(3), C–N = 1.359(4) and C=N = 1.330(4) Å).[8] The second possible but as-yet unknown electron localised donor type,[9] class **E**, replaces imino N-donation (**D**) by imino C=N electron donation. Structural traits expected for this mode would be increased non-amide M–N bond lengths relative to those of types **B** and **D**, a C=N vector near orthogonal to the metal-to-imine group approach, extension of the C=N bond due to donation of π-electron density, and a closing of the metallacyclic NMN angle relative to that observed in class **D** coordination. It is noteworthy that metal amidinate π-interactions are limited to a handful of electron deficient 16e ruthenium complexes,[10–13] *e.g.* **4** and **5** (Fig. 2), and it is therefore unsurprising that examples of coordination class **E** are absent from the structural database.

Our interest in amidinate chemistry stems from our use of bulky *N,N′*-di(aryl)amidinates $\{ArNC(R)NAr\}^-$ (Ar = 2,6-dialkylphenyl or 2,4,6-trialkylphenyl, R = H, alkyl or aryl) to kinetically stabilise group 13 hydride complexes,[14,15] sterically engineer carbon–fluorine bond activation[16,17] or act as anionic ligand supports for group 2[18,19] and low valent compounds.[17,20] Accordingly, we have investigated many aspects of s-, p- and f-block amidinate chemistry and reported several new and exciting amidinate binding modes.[21–29] We now extend our structural discussion of lithium *N,N′*-di(aryl)formamidinates [Li{ArNC(H)NAr}] (Ar = 2,6-$R_2C_6H_3$, R = Me, Et or ^{i}Pr)[30] to complexes containing the triamine donor

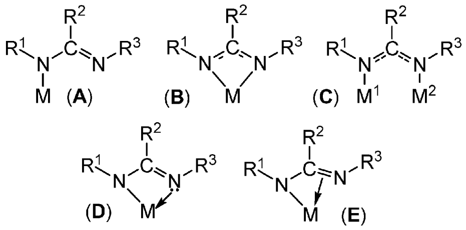

Fig. 1 The three common amidinate coordination classes **A–C** and two N,N′-asymmetric subclasses of type **B**: **D** and **E**. (Note: Only *E-anti* isomer of class **A** is displayed, other isomers, *e.g.* *E-syn* are possible).

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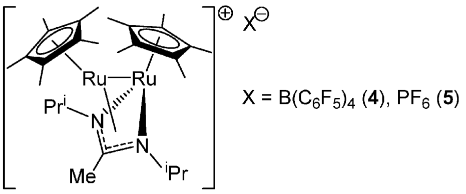


Fig. 2 Representative examples of metal amidinate coordination using π-conjugate electrons.

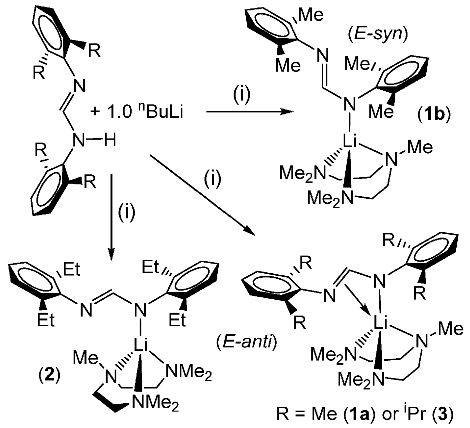
N,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdeta) and report compelling evidence for metal amidinate species with η^2:η^1-C$=$N,N′ binding; the first examples of class **E** coordination.

Results and discussion

The 1 : 1 stoichiometric treatment of ArNC(H)N(H)Ar with *n*-butyl lithium in THF/pmdeta solution results in clean deprotonation of the *N*,*N*′-di(aryl)formamidine amino group, indicated by the absence of a N–H stretch in the respective FTIR spectra,[31] to afford colourless crystalline compounds of general formula [Li{ArNC(H)NAr}(pmdeta)], where Ar = 2,6-$R_2C_6H_3$ (R = Me (**1**), Et (**2**) or ^{i}Pr (**3**)) (Scheme 1). Unlike the parent *N*,*N*′-di(aryl)formamidines, which exhibit fluxional ^{1}H NMR spectra at ambient temperature due to interconversion between *Z-anti*/*E-syn* and *E-anti*[32] isomers,[31] compounds **1–3** display resonances consistent with a single N,N′-symmetric amidinate isomer. Aside from this, the most noteworthy aspect of these spectra is the upfield shift of the formamidinate NC(*H*)N resonances from 6.82, 6.89 and 7.02 ppm, respectively, for the *Z*-anti parent formamidines (C_6D_6)[31] to 7.78 (**1**), 7.63 (**2**) and 7.98 ppm (**3**). This shift is accompanied by a related shift in the ^{13}C{^{1}H} NMR N*C*(H)N resonance from *ca.* 145 ppm to 162.6 (**1**), 163.7 (**2**) and 164.1 ppm (**3**).[31] This data compares well to the related four coordinate N,N′-symmetric lithium compound [Li{(2,6-^{i}Pr$_2C_6H_3$)NC(H)N(2,6-^{i}Pr$_2C_6H_3$)}(THF)$_2$] (**6**), whose respective ^{1}H NMR NC(*H*)N resonance is at 7.89 ppm and ^{13}C NMR N*C*(H)N resonance is at 161.3 ppm.[22]

The isolation of compounds **1–3** as crystalline samples permitted X-ray structure determination‡, with N,N′-symmetric four or five coordinate lithium complexes being the predicted outcome on the basis of spectroscopic data. The molecular structures of compounds **1**, **2** and **3** are shown in Fig. 3, Fig. 4 and Fig. 5, respectively, with crystallographic parameters compiled in Table 1 and selected bond lengths and angles in Table 2.

Contrary to the symmetrical coordination modes predicted on the basis of NMR data (see above), the solid state structures of lithiated ArNC(H)N(H)Ar compounds **1–3** exhibit two isomeric/tautomeric forms, both with asymmetric nitrogen environments. Compound **1** possesses two unique molecular units in the asymmetric unit, one displaying *E-anti*[32] isomerism for the amidinate ligand (herein referred to as **1a**, see Fig. 3(a)) and the other *E-syn* isomerism (**1b**, see Fig. 3(b)). Compounds **2** and **3** crystallise with a single *E-anti* lithium amidinate in the asymmetric unit. As summarised in Table 2, all four [Li(ArNC(H)N(H)Ar)(pmdeta)] structures (two for compound **1**) display either a single short Li–N contact and type **A** coordination (see Fig. 1, 1.976(4) (**1b**) and 1.956(11) Å (**2**)) or a longer primary Li–N contact (2.034(4) (**1a**) and 2.029(3) Å (**3**)) with a second extended Li–N contact within the range of reported Li–N$_{\text{amidinate}}$ bonds (1.927(5)–2.664(4) Å)[33] as per type **D** coordination (2.560(5) (**1a**) and 2.626(3) Å (**3**)). The increased steric congestion of **1a** and **3** is manifested in extensions of the Li–N$_{\text{pmdeta}}$ contacts relative to those of **1b** and **2** (see Table 2). This is particularly pronounced for the central N$_{\text{pmdeta}}$-donor; 2.209(5) (**1a**), 2.072(4) (**1b**), 2.074(11) (**2**) and 2.210(3) Å (**3**). It is noteworthy that the three reported examples of lithium imidinates/amidinates coordinated by pmdeta[34] display a similar trend in central Li–N$_{\text{pmdeta}}$ bond lengths, and that this is representative of lithium coordination number. For example, the four coordinate lithium imidinate [Li{N$=$C(Ph)N(H)C(Ph)$=$C(H)(3-NC_5H_5)}(pmdeta)][34a] displays Li–N$_{\text{imide}}$ and central Li–N$_{\text{pmdeta}}$ bond lengths of 1.963(8) Å and 2.093 Å, respectively, while the five coordinate lithium benzamidinate [Li{PhNC(Ph)NPh}(pmdeta)][34c] displays extended Li–N$_{\text{amide}}$ and central Li–N$_{\text{pmdeta}}$ bond lengths of 2.076(6) and 2.235(6) Å, respectively. Aside from the steric bulk of the ligands, which ensure a monomeric composition, steric arguments cannot be made to explain the bonding observed in compounds **1–3**, *i.e.* complexes bearing the least and most sterically demanding amidinates display analogous bonding. Instead, it is likely that crystal packing effects dominate.



Scheme 1 Conditions: (i) THF/pmdeta solution, room temperature, 15 h, −1.0 equiv. ^{n}BuH. Note: Compound **1** crystallises with two isomers, **1a** and **1b**, in the crystallographic asymmetric unit.

Monometallic compounds bearing chelated NCN-asymmetric amidinates (Fig. 1, **D**) typically display a planar MNCN

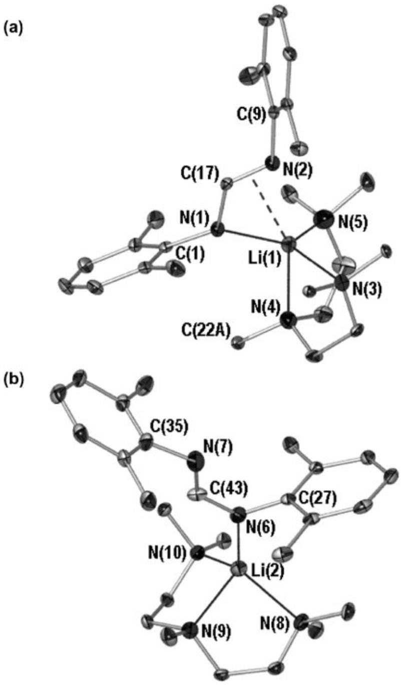


Fig. 3 Molecular structures (POV-Ray illustration, 40% thermal ellipsoids) of the two molecular units in the asymmetric unit of **1**; (a) *E-anti* formamidinate (**1a**), (b) *E-syn* formamidinate (**1b**). All hydrogen atoms are omitted for clarity and, where disorder is present, the highest occupancy atoms are displayed. Selected bond lengths and angles are listed in Table 2.

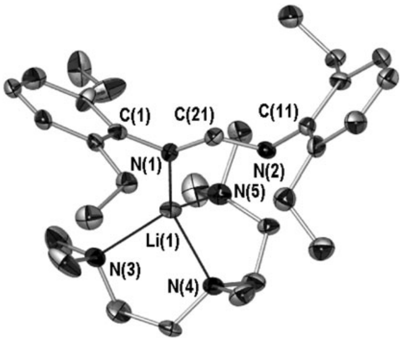


Fig. 4 Molecular structure of **2** (POV-Ray illustration, 40% thermal ellipsoids). All hydrogen atoms are omitted for clarity and, where disorder is present, the highest occupancy atoms are displayed. Selected bond lengths and angles are listed in Table 2.

Table 1 Summary of crystal data for compounds **1–3**

	Compound **1**	Compound **2**	Compound **3**
Formula	$C_{52}H_{84}Li_2N_{10}$	$C_{30}H_{50}LiN_5$	$C_{34}H_{58}LiN_5$
Formula weight	863.17	487.69	543.79
Temperature/K	123(2)	123(2)	123(2)
Space group	P_n	$P2_1/n$	$P2_12_12_1$
a/Å	8.6759(2)	13.889(3)	11.7197(2)
b/Å	17.6854(4)	15.094(3)	16.5509(2)
c/Å	17.4137(5)	15.379(3)	17.5383(2)
α (°)	90	90	90
β (°)	102.146(2)	111.31(3)	90
γ (°)	90	90	90
Volume/Å^3	2612.09(11)	3003.6(10)	3401.93(9)
Z	2	4	4
D_c/g cm^{-3}	1.097	1.078	1.062
μ/mm^{-1}	0.065	0.063	0.062
Reflections collected	23881	11714	31582
Unique reflections	10868	5646	8298
Parameters varied	675	366	374
R(int)	0.0684	0.1647	0.0985
R_1	0.0559	0.0924	0.0514
wR_2	0.1228	0.1932	0.0983

metallacycle, like those of **1a** and **3**, in which lithium deviates from the NCN plane by 0.18(1) and 0.015(7) Å, respectively, with negligible evidence of M–C contact. An example of this can be seen in the compound $[Sb\{N^iPrC(NH^iPr){=}N^iPr\}\{C(N^iPr)_2{=}N^iPr\}]$ (Sb–N$_{amido}$ = 2.069(6), Sb–N$_{imino}$ = 2.227(6) Å),[35] in which the antimony-to-carbon contact is beyond the combined van der Waals/ionic radii (Sb–C = 2.621 Å, combined radii = 2.18 Å).[36] For bimetallic systems in which one or both nitrogens chelate, M–C bonding is usually not observed, although there are some notable exceptions to this,[26,29,37–39] particularly where π-donation occurs (*e.g.* **4** and **5**, Fig. 2).[10–13] Furthermore, where an amidinate coordinates in a monodentate fashion (Fig. 1, **A**), the backbone NCN C–N bond lengths are typically representative of discrete single and double bonds; an appropriate example being the bulky lithium benzamidinate compound $[Li\{^iPrNC(2,6\text{–}\{2,4,6\text{-}^iPr_3C_6H_2\}_2C_6H_3){=}N^iPr\}(tmeda)]$,[40] which displays a *Z-anti* amidinate structure with NCN carbon nitrogen lengths of 1.361(5) and 1.309(5) Å. For the monodentate amidinate compound **1b** (*E-syn* isomer, Fig. 3b) a similar disparity in C–N bond lengths occurs; 1.343(3) and 1.262(3) Å (parent amidine: 1.335(4) and 1.286(3) Å).[31] For the *E-anti*[32] compound **2**, in which a lithium-to-imino nitrogen distance of 3.388(15) Å clearly precludes coordination, the difference in NCN C–N bond lengths is less pronounced (1.295(7) and 1.316(7) Å (parent amidine: 1.281(3) and 1.352(3) Å).[31] However, the combined NCN C–N bond lengths of these two species are statistically identical (2.611(14) (**2**) and 2.605(6) Å (**1b**)). By contrast, **1a** displays appreciable extension of its combined NCN bond length (2.637(6) Å), despite decreased amidinate bulk relative to **2**. This is accompanied by the appearance of a lower frequency C=N stretching mode in the FTIR spectrum of **1**, indicating bond weakening (**1**: FTIR C=N stretching bands at 1649 (w), 1601 (s) and 1549 (s) cm^{-1}; **2**: FTIR C=N stretching bands at 1654 (s) and 1589 (s) cm^{-1}). Similar observations can be made for **3** (combined NCN C–N 2.640(4) Å), although the FTIR data is less indicative of bond weakening (**3**: FTIR C=N stretching bands at 1664 (s), 1596 (s) and 1538 (s) cm^{-1}). The C–N bond structural phenomena may be rationalised on the basis of increased steric bulk at lithium, brought about by the proximity of the C=N(Ar) group (NCN angle: 123.3(2) (**1a**), 129.1(3) (**1b**), 126.4(7) (**2**) and 122.01(15)° (**3**)), as is borne out by the relative increase in pmdeta Li–N bond lengths for **1a** and **3** *vs.* **1b** and **2** (see Table 2). However, two aspects of this steric effect are unusual (see Fig. 6 for illustrative bonding comparison of **1a** and **2**). Firstly, the greatest increase in Li–N bond lengths occurs for the central pmdeta donor, *e.g.* 2.209(5) (**1a**) and 2.072(4) Å (**1b**), and not the Li–N$_{pmdeta}$ bonds that are closer to the amidinate (*e.g.* 2.187(5) (**1a**) and 2.172(4) Å (**1b**)). This is particularly unusual as the former bond provides the closest Li–N$_{pmdeta}$ contact for **1a** and **2**. Secondly, the metal-to-carbon distances in **1a** and **3** are within the upper

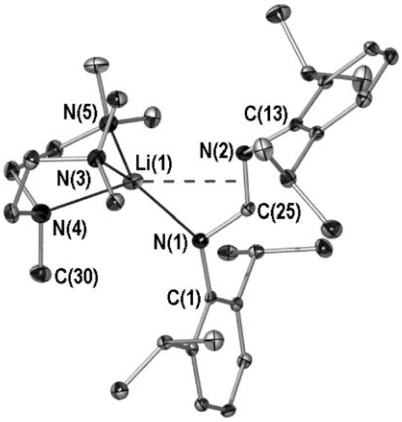


Fig. 5 Molecular structure of **3** (POV-Ray illustration, 40% thermal ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths and angles are listed in Table 2.

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1–3**

	1a (*E-anti*)	**1b** (*E-syn*)	**2** (*E-anti*)	**3** (*E-anti*)
Li–N$_{amido}$	2.034(4)	1.976(4)	1.956(11)	2.029(3)
Li–N$_{imino}$	2.560(5)	—	3.388(15)	2.626(3)
Li–C$_{NCN}$	2.608(5)	—	2.848(20)	2.663(4)
Li–centre of C=N	2.448(15)	—	2.991(20)	2.596(13)
NCN C–N	1.330(3)	1.343(3)	1.316(7)	1.327(2)
NCN C=N	1.307(3)	1.262(3)	1.295(7)	1.313(2)
NCN C–N + C=N	2.637(6)	2.605(6)	2.611(14)	2.640(4)
Li–N(CH$_3$)$_2$	2.177(4)	2.157(4)	2.124(11)	2.206(3)
Li–N(CH$_3$)$_2$	2.187(5)	2.172(4)	2.161(11)	2.226(3)
Li–N(CH$_3$)	2.209(5)	2.072(4)	2.074(11)	2.210(3)
N$_{amido}$–Li–N$_{imino}$	59.65(15)	—	48.5(4)	57.79(9)
N$_{amido}$–C–N$_{imino}$	123.3(2)	129.1(3)	126.4(7)	122.01(15)
N(CH$_3$)$_2$–Li–N(CH$_3$)$_2$	114.26(18)	116.42(18)	116.0(5)	117.63(14)
N(CH$_3$)$_2$–Li–N(CH$_3$)	83.12(15)	87.96(16)	87.3(4)	81.80(12)
N(CH$_3$)$_2$–Li–N(CH$_3$)	83.06(16)	87.15(16)	86.1(4)	81.35(12)
N$_{amido}$–Li–N(CH$_3$)	109.56(19)	117.4(2)	126.6(5)	118.11(3)
N$_{imino}$–Li–N(CH$_3$)	168.6(3)	—	88.6(4)	174.61(15)
N(CH$_3$)–Li–C=N$_{cent}$	154.6(4)	—	99.8(5)	162.6(3)
Angle of Li–C=N$_{cent}$ vector intercept to C=N vector	84.3(14)	—	72.0(21)	88.1(10)

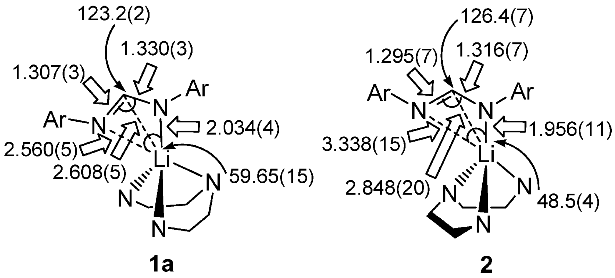


Fig. 6 Diagram illustrating atomic contact (Å) and angle (°) differences between **1a** and **2**. 2,6-alkylaryl groups are represented as 'Ar', pmdeta methyl groups are omitted and non-bonding contacts are represented as hatched lines.

range of literature Li–C interactions, such as those in [$LiZr\{CCSi^tBu_4\}_5(THF)_3$] (2.329(14)–2.996(15) Å)[41] and [$BPh_3\{CN(Li)C_2H_2N(CH_3)\}$] (2.393(4)–2.982(4) Å),[42] without protrusion of the metal from the plane described by the NCN donor set (see above). To our knowledge this is unprecedented.[9] Indeed, bimetallic amidinate species displaying μ_2:η^2:η^2- or μ_2:η^2:η^1-coordination are the only metal amidinate species to display M–C contacts.[10–13,26,29,37–39] However, in contrast to **1a** and **3**, this coordination necessitates that the metal centre sits out of the N,N′-chelate plane in a similar fashion to compounds **4** and **5**. This, in tandem with the increased Li–N_{imino} bond lengths of **1a** and **3** relative to Li–N bonds in complexes displaying coordination type **B** (**6**: 2.036(4) and 2.041(4) Å; **1a**: 2.034(4) and 2.560(5) Å; **3**: 2.029(3) and 2.626(3) Å), C=N vectors that are near orthogonal to the lithium-to-imine bond approach (79.6(16) (**6**), 84.3(14) (**1a**), 72.0(21) (**2**) and 88.1(10)° (**3**)), and closing of the metallacyclic NMN angle (68.2(1) (**6**), 59.65(15) (**1a**), 48.5(4) (**2**) and 57.79(9)° (**3**)) leads us to conclude that the solid state structures of **1a** and **3** are the first examples of η^2:η^1-C=N,N′ metal amidinate coordination.

Further studies of the coordination and reactivity of bulky amidinates are under way in our respective laboratories.

Experimental

The *N*,*N*′-di(aryl)formamidinate ligand precursors *N*,*N*′-di(2,6-dimethylphenyl)-, *N*,*N*′-di(2,6-diethylphenyl)- and *N*,*N*′-di(2,6-diisopropylphenyl)formamidine were synthesised according to a modified published procedure.[43] *n*-Butyl lithium (1.6 M in hexane) was purchased from Aldrich. Tetrahydrofuran (THF) was dried over sodium, freshly distilled from sodium benzophenone ketyl and freeze–thaw de-gassed prior to use. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (pmdeta) was freshly distilled, dried over 3–5 Å molecular sieves and freeze–thaw de-gassed prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H NMR spectra were recorded at 300.13 MHz and ^{13}C NMR spectra were recorded at 75.46 MHz using a Bruker DPX 300 spectrometer, with chemical shifts referenced to the residual ^{1}H or ^{13}C resonances of the d_6-benzene solvent used. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected.

General procedure

n-Butyl lithium (2.00 cm^3, 3.20 mmol) was added dropwise to a stirred solution of *N*,*N*′-di(aryl)formamidine (3.20 mmol) in THF (20 cm^3) and pmdeta (3.00 cm^3). The resulting solution, which ranged from colourless to pale blue in appearance, was then stirred for 15 h. Filtration and concentration to the point of crystallisation gave colourless prismatic samples of compounds **1–3** upon standing. These were devoid of FTIR absorbances and ^{1}H NMR resonances attributable to the parent *N*,*N*′-di(aryl)formamidine. Relevant details for each compound are as follows:

[$Li\{N(2,6\text{-}Me_2C_6H_3)C(H)N(2,6\text{-}Me_2C_6H_3)\}(pmdeta)$] (1)

Yield 1.13 g (82%), m.p. 135 °C. ^{1}H NMR (C_6D_6, 300 K): δ 1.87 (s, 12 H, N(CH_3)$_2$), 2.02 (br m, 8 H, NCH_2), 2.14 (s, 3 H, N(CH_3)), 2.38 (s, 12 H, 2,6-CH_3), 6.90 (m, 2 H, *p*-Ar-*H*), 7.15 (m, 4 H, *m*-Ar-*H*) and 7.78 (s, 1 H, NC(*H*)N). ^{13}C NMR (C_6D_6, 300 K): δ 19.0 (s, 2,6-CH_3), 42.9 (s, NCH_2), 44.4 (s, N(CH_3)$_2$), 53.9 (s, NCH_2), 56.5 (s, N(CH_3)), 119.3, 127.5, 130.1, 152.8 (s, Ar–*C*) and 162.6 (s, N*C*(H)N). IR (Nujol)/cm^{-1}: 2016 (w), 1913 (m), 1884 (w), 1849 (w), 1822 (w), 1788 (w), 1762 (w), 1727 (w), 1649 (w), 1601 (s), 1549 (s), 1331 (m), 1302 (m), 1250 (s), 1194 (m), 1169 (br w), 1156 (m), 1112 (m), 1093 (s), 1060 (w), 1033 (s), 1000 (w), 983 (m), 932 (m), 921 (w), 903 (m), 822 (w), 789 (w), 768 (m), 755 (m), 730 (w), 670 (w) and 591 (w).

[$Li\{N(2,6\text{-}Et_2C_6H_3)C(H)N(2,6\text{-}Et_2C_6H_3)\}(pmdeta)$] (2)

Yield 1.16 g (74%), m.p. 75 °C. ^{1}H NMR (C_6D_6, 300 K): δ 1.04 (br m, 12 H, 2,6-CH_2CH_3), 1.79 (br m, 8 H, NCH_2), 1.89 (s, 12 H, N(CH_3)$_2$), 2.05 (s, 3 H, N(CH_3)), 2.66 (br m, 8 H, 2,6-CH_2CH_3), 6.73–6.99 (m, 6 H, Ar-*H*) and 7.63 (s, 1 H, NC(*H*)N). ^{13}C NMR (C_6D_6, 300 K): δ 15.0 (s, 2,6-CH_2CH_3), 24.3 (s, 2,6-CH_2CH_3), 41.9 (s, NCH_2), 44.5 (s, N(CH_3)$_2$), 52.7 (s, NCH_2), 56.9 (s, N(CH_3)), 119.2, 125.0, 136.3, 151.6 (s, Ar-*C*) and 163.7 (s, N*C*(H)N). IR (Nujol)/cm^{-1}: 3177 (w), 2494 (w), 2363 (w), 1905 (w), 1885 (w), 1835 (w), 1785 (w), 1735 (w), 1654 (s), 1589 (s), 1539 (s), 1333 (w), 1293 (m), 1263 (m), 1192 (m), 1147 (m), 1122 (m), 1097 (m), 1032 (s), 936 (m), 891 (w), 861 (m), 796 (s) and 755 (m).

[$Li\{N(2,6\text{-}^iPr_2C_6H_3)C(H)N(2,6\text{-}^iPr_2C_6H_3)\}(pmdeta)$] (3)

Yield 1.16 g (67%), m.p. 149 °C. ^{1}H NMR (C_6D_6, 300 K): δ 1.40 (d, 24 H, 2,6-CH(CH_3)$_2$, $^3J_{HH}$ = 7.0 Hz), 1.87 (br m, 8 H, NCH_2), 2.02 (s, 12 H, N(CH_3)$_2$), 2.09 (s, 3 H, N(CH_3)), 3.87 (sept., 4 H, 2,6-C*H*(CH_3)$_2$, $^3J_{HH}$ = 7.0 Hz), 7.14 (m, 2 H, *p*-Ar-*H*), 7.31 (m, 4 H, *m*-Ar-*H*) and 7.97 (s, 1 H, NC(*H*)N). ^{13}C NMR (C_6D_6, 300 K): δ 23.8 (s, 2,6-CH(CH_3)$_2$), 26.5 (s, 2,6-*C*H(CH_3)$_2$), 42.7 (s, NCH_2), 44.2 (s, N(CH_3)$_2$), 53.1 (s, NCH_2), 55.9 (s, N(CH_3)), 120.2, 121.9, 141.3, 149.5 (s, Ar-*C*) and 164.1 (s, N*C*(H)N). IR (Nujol)/cm^{-1}: 1897 (m), 1843 (m), 1787 (w), 1664 (s), 1596 (s), 1538 (s), 1300 (s), 1255 (m), 1228 (m), 1174 (m), 1099 (m), 1072 (w), 1054 (w), 1032 (s), 990 (m), 935 (s), 917 (m), 897 (w), 819 (w), 800 (s), 790 (w), 778 (w), 766 (w), 756 (s) and 672 (w).

X-Ray crystallography

Crystalline samples of compounds **1–3** were mounted in viscous hydrocarbon oil on glass fibres at −150 °C (123 K). Crystal data were obtained using an Enraf-Nonius Kappa CCD diffractometer. X-Ray data were processed using the DENZO program.[44] Structural solution and refinement was carried out using the SHELX suite of programs[45,46] with the graphical interface X-Seed.[47] All hydrogen atoms were placed in calculated positions using the riding model. Crystal data and refinement parameters are compiled in Table 1 with selected bond lengths and angles provided in Table 2.

For compound **1**, the molecular unit **1a** in the asymmetric unit displays disorder of the pmdeta ligand. This disorder concerns carbon atoms of the N(CH_3)$_2$ groups and ethylene linkers. Modelling of this disorder over two sites of partial occupancy was attempted successfully for all atoms affected. The determined occupancies as are follows. C18 and C19 of the N(CH_3)$_2$ group: 58 : 42%, C20 and C21 of ethylene linker:

58 : 42%, C23 and C24 of ethylene linker: 62 : 38%, C25 and C26 of $N(CH_3)_2$ group: 60 : 40%.

For compound **2**, one methyl of an ethyl group, C8, is disordered. This was modelled successfully over two sites of partial occupancy (67 : 33%). As per **1a**, the pmdeta ligand of **2** also exhibits disorder. Two carbons, one from a $N(CH_3)_2$ group and the other from a linking ethylene (C29 and C28 respectively), were successfully modelled with the partial occupancies 56 : 44 and 50 : 50%, respectively.

Compound **3** was refined in the chiral space group $P2_12_12_1$ with a Flack parameter of −1.5(17) and no correlation matrix elements larger than 0.500. Refinement of the inverted structure gave a Flack parameter of 2.4(17).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.‡

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References

1 (*a*) For a recent review of metal organoamide chemistry see: R. Kempe, *Angew. Chem., Int. Ed.*, 2000, **39**, 468; (*b*) For a review of amidinate chemistry see: J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.

2 The Cambridge Structural Database (CSD, version 5.26, November 2004) contains over 2000 structures containing a metal coordinated amidinate $[R^1NC(R^2)NR^3]^-$, heteroatom (E) substituted amidinate $[R^1NC(R^2)ER^3]^-$, or guanidinate $[R^1NC(NR^2_2)NR^3]^-$ ligand.

3 Examples: (*a*) D. M. Grove, G. van Koten, H. J. C. Ubbels, K. Vrieze, L. C. Niemann and C. H. Stam, *J. Chem. Soc., Dalton Trans.*, 1986, 717; (*b*) A. Zinn, K. Dehnicke, D. Fenske and G. Baum, *Z. Anorg. Allg. Chem.*, 1991, **596**, 47; (*c*) S. R. Foley, C. Bensimon and D. S. Richeson, *J. Am. Chem. Soc.*, 1997, **119**, 10359.

4 Examples: (*a*) J. A. R. Schmidt and J. Arnold, *Organometallics*, 2002, **21**, 2306; (*b*) E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2000, 497; (*c*) F. A. Cotton, L. M. Daniels, C. A. Murillo and P. Schooler, *J. Chem. Soc., Dalton Trans.*, 2000, 2001.

5 Examples: (*a*) W.-Z. Chen and T. Ren, *Inorg. Chem.*, 2003, **42**, 8847; (*b*) F. A. Cotton, J. P. Donahue and C. A. Murillo, *J. Am. Chem. Soc.*, 2003, **125**, 5436; (*c*) F. A. Cotton, L. M. Daniels, P. Huang and C. A. Murillo, *Inorg. Chem.*, 2002, **41**, 317.

6 From a survey of the Cambridge Structural Database (CSD, version 5.26, November 2004), there are 14 reported examples of metal N,N′-symmetrical amidinates with type **A** coordination.

7 M. P. Coles, D. C. Swenson, R. F. Jordan and V. G. Young, *Organometallics*, 1997, **16**, 5183.

8 T.-G. Ong, G. P. A. Yap and D. S. Richeson, *Chem. Commun.*, 2003, 2612.

9 There are no examples of metal amidinate complexes bearing ligands of type $[R^1NC(R^2)NR^3]^-$ (where R^1 and R^3 = alkyl, aryl or silyl, and R^2 = H, alkyl, aryl, amido, phosphido or silyl) that possess $M–N_{imino}$ bond lengths greater than $M–N_{amido}$ with appreciable contact to the imino carbon and/or a shorter $M–CN_{centroid}$ contact than the $M–N_{imino}$ distance.

10 H. Kondo, K. Matsubara and H. Nagashima, *J. Am. Chem. Soc.*, 2002, **124**, 534.

11 H. Kondo, Y. Yamaguchi and H. Nagashima, *J. Am. Chem. Soc.*, 2001, **123**, 500.

12 Y. Yamaguchi and H. Nagashima, *Organometallics*, 2000, **19**, 725.

13 T. Hayashida, Y. Yamaguchi, K. Kirchner and H. Nagashima, *Chem. Lett.*, 2001, 954.

14 R. J. Baker, C. Jones, P. C. Junk and M. Kloth, *Angew. Chem., Int. Ed.*, 2004, **43**, 3852.

15 M. L. Cole, C. Jones, P. C. Junk, M. Kloth and A. Stasch, *Chem.–Eur. J.*, 2005, **11**, 4482.

16 M. L. Cole, G. B. Deacon, P. C. Junk and K. Konstas, *Chem. Commun.*, 2005, 1581.

17 M. L. Cole and P. C. Junk, *Chem. Commun.*, 2005, 2695.

18 R. T. Boere, M. L. Cole and P. C. Junk, *New J. Chem.*, 2005, 128.

19 M. L. Cole and P. C. Junk, *New J. Chem.*, 2005, 135.

20 C. Jones, P. C. Junk, J. A. Platts, D. Rathmann and A. Stasch, *Dalton Trans.*, 2005, 2497.

21 R. T. Boere, M. L. Cole, P. C. Junk, J. D. Masuda and G. Wolmerhauser, *Chem. Commun.*, 2004, 2564.

22 M. L. Cole, A. J. Davies, C. Jones and P. C. Junk, *J. Organomet. Chem.*, 2004, **689**, 3093.

23 J. Baldamus, C. Berghof, M. L. Cole, E. Hey-Hawkins, P. C. Junk and L. M. Louis, *Eur. J. Inorg. Chem.*, 2002, 2878.

24 M. L. Cole, P. C. Junk and L. M. Louis, *J. Chem. Soc., Dalton Trans.*, 2002, 3906.

25 M. L. Cole, D. J. Evans, P. C. Junk and L. M. Louis, *New J. Chem.*, 2002, 1015.

26 J. Baldamus, C. Berghof, M. L. Cole, D. J. Evans, E. Hey-Hawkins and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, 2002, 4185.

27 J. Baldamus, C. Berghof, M. L. Cole, D. J. Evans, E. Hey-Hawkins and P. C. Junk, *J. Chem. Soc., Dalton Trans.*, 2002, 2802.

28 M. L. Cole and P. C. Junk, *J. Organomet. Chem.*, 2003, **666**, 55.

29 M. L. Cole, D. J. Evans, P. C. Junk and M. K. Smith, *Chem.–Eur. J.*, 2003, **9**, 415.

30 Refer to refs. 22–25 and ref. 29 for our previous studies of lithiated *N*,*N*′-di(aryl)formamidinates.

31 R. T. Boere, M. L. Cole, P. C. Junk and E. G. Robertson, unpublished data.

32 The nomenclature used to describe amidinate isomers/tautomers is that described in *The Chemistry of Amidines and Imidates*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, UK, 1991.

33 From a survey of the Cambridge Structural Database (CSD, version 5.26, November 2004), these $Li–N_{amidinate}$ contact boundaries are set by the compounds contained in the following articles. Lower limit: M. P. Coles and P. B. Hitchcock, *Chem. Commun.*, 2002, 2794. Upper limit: T. Chivers, A. Downard and G. P. A. Yap, *J. Chem. Soc., Dalton Trans.*, 1998, 2603.

34 Lithium imidate compound: (*a*) S. C. Ball, R. P. Davies, P. R. Raithby, G. P. Shields and R. Snaith, *J. Organomet. Chem.*, 1998, **550**, 457; (*b*) Lithium amidinate compounds: W. M. Boesveld, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1999, 4041; (*c*) I. Cragg-Hine, M. G. Davidson, F. S. Mair, P. R. Raithby and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1993, 2423; (*d*) J. Barker, D. Barr, N. D. R. Barnett, W. Clegg, I. Cragg-Hine, M. G. Davidson, R. P. Davies, S. M. Hodgson, J. A. K. Howard, M. Kilner, C. W. Lehmann, I. Lopez-Solera, R. E. Mulvey, P. R. Raithby and R. Snaith, *J. Chem. Soc., Dalton Trans.*, 1997, 951.

35 P. J. Bailey, R. O. Gould, C. N. Harmer, S. Pace, A. Steiner and D. S. Wright, *Chem. Commun.*, 1997, 1161.

36 E. Fluck and K. G. Heumann, *Periodic Table of the Elements*, 1991, VCH, Weinheim, Germany.

37 R. P. Davies, D. J. Linton, P. Schooler, R. Snaith and A. E. H. Wheatley, *Eur. J. Inorg. Chem.*, 2001, 619.

38 T. Gebauer, K. Dehnicke, H. Goesmann and D. Fenske, *Z. Naturforsch., B: Chem. Sci.*, 1994, **49**, 1444.

39 G. R. Giesbrecht, A. Shafir and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1999, 3601.

40 J. A. R. Schmidt and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 2002, 2890.

41 T. P. Vaid, A. S. Veige, E. B. Lobkovsky, W. V. Glassey, P. T. Wolczanski, L. M. Liable-Sands, A. L. Rheingold and T. R. Cundari, *J. Am. Chem. Soc.*, 1998, **120**, 10067.

42 D. Vagedes, G. Kehr, D. Konig, K. Wedeking, R. Frohlich, G. Erker, C. Muck-Lichtenfeld and S. Grimme, *Eur. J. Inorg. Chem.*, 2002, 2115.

43 R. M. Roberts, *J. Org. Chem.*, 1949, **14**, 277.

44 Z. Otwinowski and W. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, in *Macromolecular Crystallography. Part A. Methods in Enzymology*, ed. C. W. Carter Jr and R. M. Sweet, Academic Press, New York, 1997, vol. 276, pp. 307.

45 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.

46 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

47 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.

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‡ CCDC reference numbers 281337–281339. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511519a