# Studies of Aryl Substituent and Solvent Donor Imposed Structural Diversity in *N*,*N'*-Diarylformamidinate Complexes of Lithium[‡]

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Treatment of *N*,*N'*-bis(2,4,6-trimethylphenyl)formamidine, $(2,4,6\text{-}Me_3C_6H_2)NC(H)NH(2,4,6\text{-}Me_3C_6H_2)$ (HFMes) with *n*-butyllithium in DME leads to deprotonation of the amidine affording the dimeric compound $[\{Li(FMes)(dme)\}_2]$ (**1**). Similar treatment of the less sterically encumbered formamidine *N*,*N'*-bis(*o*-tolyl)formamidine, $(2\text{-}MeC_6H_4)NC(H)NH(2\text{-}MeC_6H_4)$ (HFTolO) in DME (1,2-dimethoxyethane) or HFMes in hexane/TMEDA (*N*,*N*,*N'*,*N'*-tetramethylethylenediamine) yields the compounds $[Li(dme)_3][Li(FTolO)_2]$ (**2**) and [Li(FMes)(tmeda)] (**3**), respectively. Both the anion of **2** and **3** are the first monomeric group 1 formamidinates to exhibit $\eta^2$-chelation in the solid state, and **3** is the first Lewis base stabilised mononuclear group 1 formamidinate complex. Complexes **1**–**3** have been characterised by spectroscopy ($^1H$ and $^{13}C$ NMR, FTIR) and X-ray crystallography, and are discussed herein vis-à-vis formamidinate binding modes exhibited by *N*,*N'*-diarylformamidinates of smaller steric size, e.g. *N*,*N'*-bis(*p*-tolyl)formamidine, $(4\text{-}MeC_6H_4)NC(H)NH(4\text{-}MeC_6H_4)$ (HFTolP).

## Introduction

The fundamental role of group 1 amido complexes, particularly those of lithium, as synthetic reagents in inorganic chemistry and strong Bronsted bases or nucleophiles in organic synthesis[1−5] has led to considerable advances in the field of metal amide chemistry.[6] Within this arena, knowledge of reagent structure both in solution and in the solid state is crucial, permitting the synthetic chemist to tailor syntheses or transformations. In both, association is to be expected due to the high polarity of the Li−N bond.[7−13] However, aggregation can be frustrated if ligands of adequate steric bulk are employed.[14]

In contrast to the actively investigated area of transition metal formamidinate chemistry (formamidinate = $[RNC(H)NR]^-$, R = aryl, alkyl, silyl),[15,16] literature detailing the full characterisation of s-block systems has been conspicuously absent.[17] As a result there is a scarcity of structural data pertaining to this class of amidinate complex, which are generally perceived as metathesis reagents, their isolation and characterisation largely being ignored. It has been suggested that this shortage of structural data, there being just one structurally authenticated lithium formamidinate complex ($[\{Li(FTolP)(Et_2O)\}_2]$), results from the facility by which group 1 formamidinates lose solvent.[18] However, to compliment the vast array of coordination modes observed for formamidinates in d-block systems we have engaged in a program of s-block metal formamidinate structural characterisation using solvent donors that either chelate or have recognised strong donor characteristics. Thus far, this has identified several group 1 diarylformamidinate bonding motifs, e.g. $\mu_2{:}\eta^2{:}\eta^1$ (in $[\{Li_2(FTolP)_2(tmeda)\}_\infty]$)[17] and $\eta^6{:}\eta^1$ (in [K(FMes)(HFMes)]),[19] that are either rare or unprecedented in transition metal chemistry. To date several known bonding motifs like discrete $\eta^2$-chelation, have not been observed in group 1 systems. Furthermore, there is potential for new binding modes, e.g. $\eta^3$-diazaallyl, as seen for $\eta^3$-*N*-aryl diarylketeneiminates,[20] where the carbon atom of the NCN backbone would interact with a metal centre that sits perpendicular to the NCN plane either as part of symmetrical NCN donation or as a discrete C=N π-donor. In order to assess the likelihood of these, and advance our study, we have now chosen to focus our attention on formamidine ligands of greater steric bulk, in this case *N*,*N'*-bis(2,4,6-trimethylphenyl)formamidine, $(2,4,6\text{-}Me_3C_6H_2)NC(H)NH(2,4,6\text{-}Me_3C_6H_2)$ (HFMes). Herein we present a preliminary lithium study employing HFMes and relate the findings to new and archival structural data.

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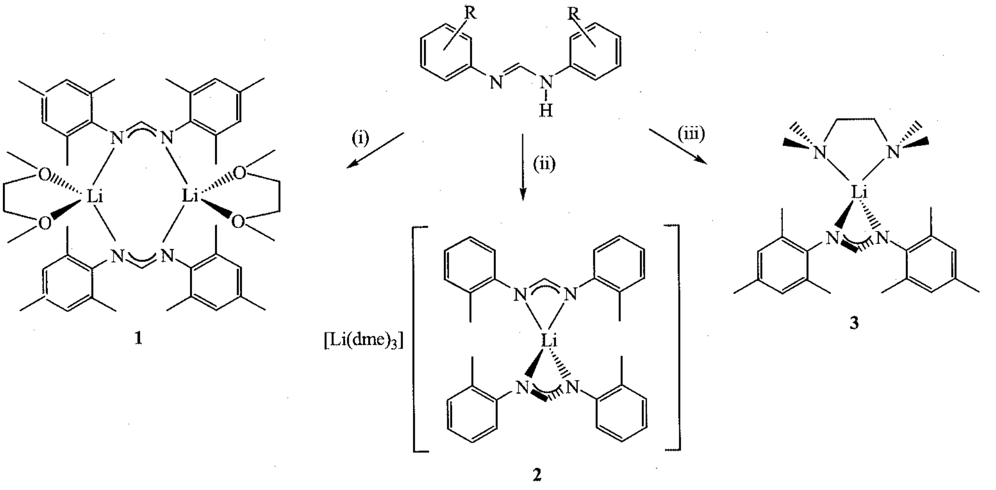

Scheme 1. Reagents and conditions: (i) R = 2,4,6-$Me_3$, 1.0 equiv. *n*BuLi, DME; (ii) R = 2-Me, 1.0 equiv. *n*BuLi, DME; (iii) R = 2,4,6-$Me_3$, 1.0 equiv. *n*BuLi, hexane/TMEDA

## Results and Discussion

Treatment of HFMes with *n*-butyllithium in the coordinating solvent DME (1,2-dimethoxyethane) results in clean deprotonation of the amino group (see Scheme 1), after moderate heating, yielding a colourless crystalline product that characterises as [Li(FMes)(dme)$_{3/2}$] (**1**) by $^1$H NMR ($C_6D_6$). Spectroscopic evidence confirms deprotonation via the absence of a resonance attributable to the amino proton of HFMes and the lack of an N−H stretch at ca. 3200−3300 cm$^{-1}$ [$^1$H NMR ($C_6D_6$): $\delta$ = 5.71 ppm (NH); FTIR: $\tilde{\nu}$ = 3228 cm$^{-1}$ (HFMes N−H stretch)].[21] The appearance of a broad NC(*H*)N resonance at $\delta$ = 7.60 ppm is also indicative of deprotonation, that of the ligand appearing at $\delta < 7.07$ ppm.[21] Similarly, the NCN backbone carbon resonance at $\delta$ = 157.6 ppm ($C_6D_6$) is suggestive of deprotonation, the analogous resonance of HFMes appearing at $\delta$ = 145.0 ppm. Attempts to obtain $^7$Li NMR spectroscopic data for **1** were thwarted by low solubility in nondonating solvents (employed to preclude further solvation). Overall, NMR resonances for **1** compare favourably to those of the FTolP ligands in the ionic complex [Li(dme)$_3$][Li$_2$($\mu_2$:$\eta^1$:$\eta^1$-FTolP)$_3$] (**4**) although the NC(*H*)N resonance is shifted to lower frequency, that of **4** appearing at $\delta$ = 8.88 ppm.[17] This intimates a differing structural preference for **1** viz. **4**, as does the abated decomposition temperature of 112 °C, which would intuitively be in excess of that for **4** were they to assume a congruent solid-state motif (**4**: dec. At 130 °C).[17]

To assess this, X-ray quality crystals of **1**, which proved extremely air-sensitive and prone to solvent loss, were isolated and a structure determination undertaken. A POV-RAY depiction of **1** can be seen in Figure 1 (30% thermal ellipsoids), whilst selected bond lengths and angles are listed in the caption. Crystallographic data for compounds **1**−**3** are listed in Table 1. Compound **1** crystallises in the monoclinic space group *P*2$_1$/*n* with half a dinuclear [{Li($\mu_2$:$\eta^1$:$\eta^1$-FMes)(dme)}$_2$] and half a DME of solvation in the asymmetric unit. Unlike **4**, compound **1** is not ionic, displaying both solvent and formamidinate coordination to

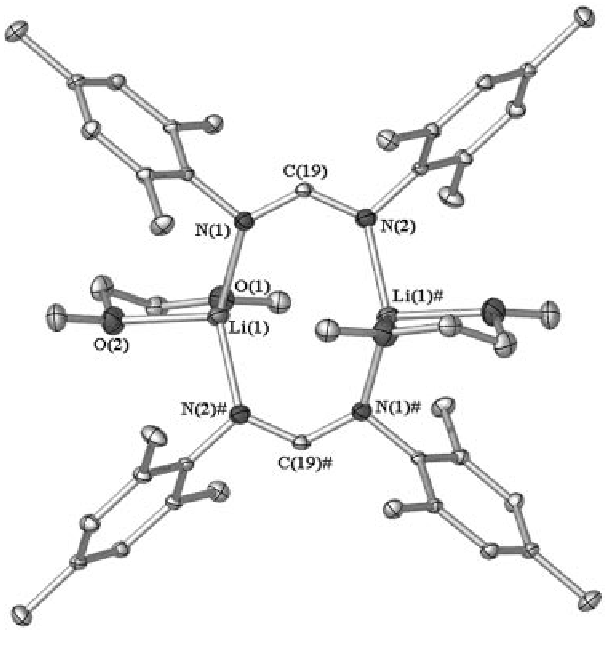

Figure 1. Molecular structure of [{Li($\mu_2$:$\eta^1$:$\eta^1$-FMes)(dme)}$_2$] (**1**), all hydrogen atoms omitted for clarity; selected bond lengths [Å] and angles [°]: N(1)−Li(1) 2.035(6), N(2)−Li(1)# 2.033(6), N(1)−C(19) 1.312(4), N(2)−C(19) 1.314(4), Li(1)−O(1) 2.043(6), Li(1)−O(2) 2.093(6), N(1)−Li(1)−N(2)# 133.5(3), O(1)−Li(1)−O(2) 78.9(2), N(1)−Li(1)−O(1) 101.4(3), N(1)−Li(1)−O(2) 111.0(3), Li(1)−N(1)−C(19) 129.7(3), N(1)−C(19)−N(2) 127.7(2), C(1) ring−NCN 66.5(3), C(10) ring−NCN 66.6(3), C(1) ring−C(10) ring 87.2(1)

Table 1. Summary of crystal data for compounds **1**−**3**

| | $[\{Li(FMes)(dme)\}_2]\cdot DME$ (**1**) | $[Li(dme)_3][Li(FTolO)_2]$ (**2**) | $[Li(FMes)(tmeda)]$ (**3**) |
|---|---|---|---|
| Empirical formula | $C_{25}H_{38}LiN_2O_3$ | $C_{42}H_{60}Li_2N_4O_6$ | $C_{25}H_{39}LiN_4$ |
| Molecular mass | 421.53 | 730.82 | 402.54 |
| Temperature [K] | 123(2) | 296(2) | 123(2) |
| Space group | $P2_1/n$ | $C2/c$ | $P\bar{1}$ |
| $a$ [Å] | 12.1580(14) | 14.28(7) | 8.2180(16) |
| $b$ [Å] | 15.6552(18) | 18.57(9) | 12.235(2) |
| $c$ [Å] | 14.4561(16) | 17.62(8) | 13.348(3) |
| α [°] | 90 | 90 | 103.84(3) |
| β [°] | 111.533(2) | 103.27(18) | 91.92(3) |
| γ [°] | 90 | 90 | 103.45(3) |
| Volume [$Å^3$] | 2559.5(5) | 4546(37) | 1261.7(4) |
| Z | 2 | 4 | 2 |
| $D_c$ [g $cm^{-3}$] | 1.035 | 1.068 | 1.060 |
| μ [$mm^{-1}$] | 0.066 | 0.070 | 0.062 |
| Reflections collected | 16124 | 9664 | 23286 |
| Reflections unique | 5801 | 3248 | 6195 |
| Parameters | 289 | 255 | 281 |
| $R_{int}$ | 0.1207 | 0.1984 | 0.0671 |
| $R_1$ | 0.0782 | 0.0698 | 0.0581 |
| $wR_2$ | 0.1665 | 0.1475 | 0.1530 |

each lithium centre. This results from the increased steric bulk of FMes with respect to FTolP, which not only inhibits discrete ion formation, as in **4**, but also precludes $\mu_2:\eta^2:\eta^1$-formamidinate coordination as seen for both $[\{Li_2(\mu_2:\eta^2:\eta^1\text{-FTolP})_2(\mu_2\text{-tmeda})\}_\infty]$ (**5**)[17] and $[\{Li(\mu_2:\eta^2:\eta^1\text{-FTolP})(Et_2O)\}_2]$,[18] the Li(1)#−N(1) distance of 3.3723(60) Å testifies to this. Interestingly, the donation of two singular DME ligands in **1** is representative of the overall steric coordination number[22] of $[Li_2(\mu_2:\eta^1:\eta^1\text{-FTolP})_2(THF)_2(\mu_2\text{-thf})]$,[17] which exhibits analogous formamidinate binding modes with one chelating and one bridging THF interaction completing each lithium coordination sphere. The lithium atoms of **1** sit in a distorted tetrahedral environment [N(1)−Li(1)−N(2)# 133.5(3)°, N(2)#−Li(2)−O(2) 115.6(3)°, O(1)−Li(1)−O(2) 78.9(2)°, whilst the Li−N bond lengths of 2.035(6) Å and 2.033(6) Å are abated relative to those deposited in the Cambridge structural database (mean 2.082 Å),[23] extended with respect to those of **4** (mean 1.992 Å)[17] and similar to those displayed by the similarly dimeric lithium amide complex $[\{Li[NHC_6H_4(o\text{-}AsMe_2)](THF)_2\}_2]$ [24] (mean 2.064 Å). As per **4**, the considerable strain involved in formamidinate bridging to two separate metal atoms has repercussions regarding ligand geometry. This includes the opening of the NCN backbone angle to 127.7(3)° (**4**: mean 123.0°) and the C(19)−N(1)−Li(1) angle to 129.7(3)° (**4**: mean 122.2°), these are in stark contrast to the comparatively acute angles of the bis($\eta^2$-chelate) complex $[Mg(FTolP)_2(THF)_2]$ (mean 117.0 and 90.14°, respectively).[25] Consequently, C(19) sits 0.023 Å out of the $N_4$ plane, whilst the Li centres sit 0.670 Å out of the $N_4$ plane [N(2)#−Li(1)−N(1) plane at 56.55(33)° to the $N_4$ plane). Given the orthogonal orientation of the FMes ligands to the lithium−lithium vector, these projections are insignificant regarding possible Li(1)/Li(1)#···C(19) interactions. Intriguingly, the structural motifs of **1** and **4** are reminiscent of the "lantern-type" structures popularised by the transition metal studies of Cotton and Murillo et al.,[15,16,26] e.g. $[Mo_2(PhNC(Ph)NPh)_4]$,[27] the lower ratio of ligand/metal resulting from the restricted space in which the formamidinate ligands can orientate themselves around the diminutive dilithium core. Conversely, unlike the close-contact-enforced metal−metal bonding observed for d-block systems, which lead to magnetic and electronic phenomena,[15,16] the metal−metal distance of complex **1** [3.508(11) Å] precludes similar interaction (**4**: mean 2.580 Å). Furthermore, the steric congestion of **1** is exemplified by the near orthogonal torsion angle of the mesityl rings to one another [87.19(12)°] and the large dihedral angles of both rings to the NCN plane [C(1) ring 66.5(3)°, C(10) ring 66.6(3)°]. These impose a differing structural motif and lower formamidinate aggregation for **1**, with respect to **4**, which necessitates augmentative DME donation to achieve an equivalent degree of coordinative saturation. Meanwhile, the formamidinate backbone N−C bond lengths of 1.312(4) and 1.314(4) Å are indicative of symmetrical amidinate ligation (**4**: mean 1.326 Å; HFTolP dimer mean C−N bonds: imino 1.294 Å and amino 1.347 Å).[17] Lastly, the symmetrical dilithium di-β-dinitrogen ligand eight-membered metallacycle exhibited by **1** is not an uncommon feature of lithium structural chemistry (22 examples),[23] however, the lithium−lithium distance described (listed above) does testify to significant steric congestion about the core, there being just two polymetallacyclic examples wherein the distance of **1** is exceeded; $[(Li\{tBuNC(tBu)NtBu\})_4]$ (max. Li···Li 3.809 Å)[28] and $[Li_2\{1,2\text{-}trans\text{-}[NC(para\text{-}Tol)N(para\text{-}Tol)]_2C_6H_{10}\}]$ (max. Li···Li 4.391 Å).[29]

If complex **1** represents double *o*-methylaryl substitution (i.e. 2,6-dimethyl) and **4** represents no *o*-methylaryl substitution, the considerable variation in the solid-state motifs of **1** and **4** invites speculation as to the likely solid-state nature of a singularly *o*-methylated *N*,*N*′-diarylformamidinate lithium complex. As such, an identical preparation to that of **1** was undertaken employing *N*,*N*′-bis(*o*-tolyl)formamidine (HFTolO), see Scheme 1. As per the synthesis of **1**, treatment of HFTolO in DME with *n*-butyllithium renders a colourless crystalline compound devoid of amino-attributable resonances or stretches ($^1$H NMR and FTIR), with a composition that indicates two formamidinate ligands to three DME molecules; $[Li(FTolO)(dme)_{3/2}]$ (**2**) ($^1$H NMR). The NC(H)N-attributable resonances of **2** at $\delta$ = 8.72 ppm and 160.4 ppm ($^1$H and $^{13}$C NMR, respectively) are representative of **4** rather than **1** ($^1$H NMR: **4**: $\delta$ = 8.88 ppm; **1**: $\delta$ = 7.60 ppm) as is the decomposition temperature of 122 °C (**1**: 112 °C; **4**: 130 °C).[17] Correspondingly, block-like crystals of **2** were grown from DME and an X-ray structure determination undertaken (Figure 2; POV-RAY illustration, 30% thermal ellipsoids, relevant bond lengths and angles listed in the caption).

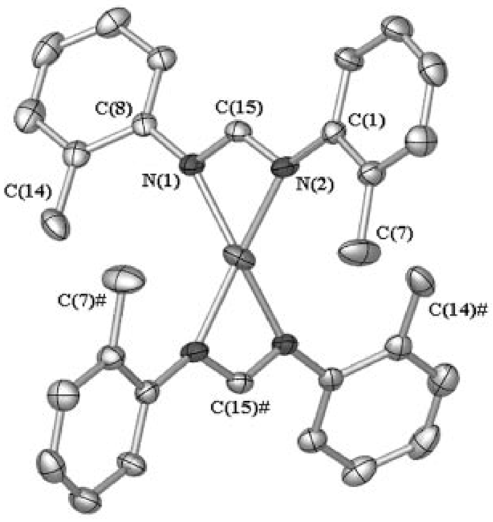

Figure 2. Molecular structure of the anion of **2** $[Li(\eta^1:\eta^1\text{-FTolO})_2]$, all hydrogen atoms omitted for clarity; selected bond lengths [Å] and angles [°]: N(1)−Li(1) 2.063(11), N(2)−Li(1) 2.073(10), N(1)−C(15) 1.323(8), N(2)−C(15) 1.315(8), N(1)−Li(1)−N(1)# 135.5(8), N(1)−Li(1)−N(2)# 130.7(3), N(1)−Li(1)−N(2) 67.3(3), N(1)−C(15)−N(2) 120.6(7), NCN−NCN# 82.5(4), C(1) ring−NCN 13.3(7), C(8) ring−NCN 33.1(6), C(1) ring−C(8) ring 28.0(4)

Akin to complex **4**, compound **2** crystallises in the space group *C*2/*c* as discrete anions and cations, of which there is half an anion/cation pair in the asymmetric unit. The cationic lithium unit, which is solvated by three DME molecules to form a distorted octahedron (mean O−Li−O bite 76.34°), is not uncommon,[23] structurally unexceptional and will not be discussed further. However, the anion (see Figure 2) is a mononuclear $[Li(FTolO)_2]$ unit that presents two $\eta^2$-FTolO ligands forming a distorted tetrahedral geometry about a lithium centre without solvent interaction [N(1)−Li(1)−N(2) bite 67.3(3)°, N(1)−Li(1)−N(1)# 135.5(8)°]. The Li−N bond lengths vary in the range 2.063(11)−2.073(10) Å and are therefore closer to the mean average Li−N bond length deposited in the Cambridge structural database (2.082 Å)[23] than the appropriate bonds of **1** and **4**. This perhaps results from lessened steric strain and the absence of bridging interactions. Likewise, the NCN backbone angle of 120.6(7)° bares a closer resemblance to the analogous angles of $[Mg(FTolP)_2(THF)_2]$ (mean: 117.0 Å),[25] than those of **1** [127.7(3)°] due to the chelate motif described. The depreciated tolyl−tolyl steric buttressing described by **2** vis-à-vis **1** can be seen in the dihedral angle of either tolyl ring to the NCN backbone plane [C(1) ring 13.3(7)°, C(8) ring 33.1(6)°] and the relative torsion angle of 28.0(4)°. Thus, in complex **2** we can state that whilst the imposition of two *o*-methyl groups upon the formamidinate frame, as in FMes, results in nonionic **1**, the addition of a singular *o*-methyl group renders an ionic complex, similar to **4**, with lower anion aggregation. This modification creates a complex devoid of formamidinate bridging interactions, which cannot merely result from *o*-methyl addition relative to **4** because complex **1** exhibits similar $\mu_2$:$\eta^1$:$\eta^1$ interactions. To rationalise this, it appears that the relative cation and anion sizes of **2** and **4** are comparable, thereby presenting lattice energies of adequate magnitude for salt formation. Meanwhile, an ionic composition for complex **1** is thermodynamically unfavourable due to the sheer steric bulk of the included amidinate ligands. These create a cation/anion size disparity. This has precedent in group 1 cyclopentadienide crown ether chemistry[30,31] where the ionic complex $[K\{15\text{-crown-}5\}_2][Cp]$ forms whilst use of 18-crown-6 yields solely the monomer [K(18-crown-6)Cp].[32] Irrespective, it remains that the ionic nature of **2** introduces a new type of lithium-based formamidinate anion.

To increase the steric encumbrance observed for complex **1**, and thereby potentially frustrate bridging interactions and generate new bonding motifs, a bulkier solvent donor; *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was utilised in a preparative procedure similar to that for **1** using hexane as solvent. Treatment of HFMes with *n*-butyllithium in hexane resulted in instant deposition of an insoluble colourless material, presumably polymeric in nature, which dissolved upon addition of excess TMEDA (see Scheme 1). Subsequent recrystallisation of the reaction mother liquor yielded colourless prisms that characterised as [Li(FMes)(tmeda)] (**3**) by $^1$H NMR, and were devoid of the resonances and stretches (NMR and FTIR, respectively) attributable to the HFMes ligand. Unlike compounds **1** and **2**, compound **3** appears to be stable to solvent loss but is extremely air-sensitive decomposing to a dark brown material upon brief exposure to air. Solid samples of **3** are thermally robust decomposing above 145 °C (cf. **1**: 112 °C; **2**: 122 °C; **4**: 130 °C).[17] The spectroscopic data for **3** bare a resemblance to those of both **4** and the related TMEDA compound $[\{Li_2(\mu_2:\eta^2:\eta^1\text{-FTolP})_2(\mu_2\text{-tmeda})\}_\infty]$ (**5**) in that compound **3** possesses a $^1$H NMR resonance at $\delta$ = 8.02 ppm (**4**: $\delta$ = 8.88 ppm; **5**: $\delta$ = 8.25 ppm, respectively);[17] however, the solvent/formamidinate ligand ratios of 1:1 mitigate against a solid-state motif analogous to **5** unless half an equivalent of TMEDA is contained as lattice solvent. In order to evaluate the above, an X-ray structure determination of **3** was undertaken (Figure 3; POV-RAY illustration, 30% thermal ellipsoids, selected bond lengths and angles listed in the caption).

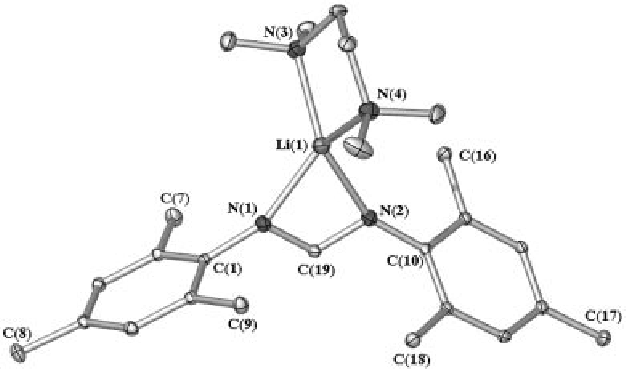

Figure 3. Molecular structure of [Li($\eta^1$:$\eta^1$-FMes)(tmeda)] (**3**), all hydrogen atoms omitted for clarity; selected bond lengths [Å] and angles [°]: Li(1)−N(1) 2.036(3), Li(1)−N(2) 2.011(3), Li(1)−N(3) 2.087(3), Li(1)−N(4) 2.057(3), N(1)−C(19) 1.314(2), N(2)−C(19) 1.328(2), $NLiN_{FMes}$−$NLiN_{TMEDA}$ 72.95(6), N(1)−Li(1)−N(2) 68.84(10), N(3)−Li(1)−N(4) 86.94(12), N(1)−Li(1)−N(3) 125.52(15), N(2)−Li(1)−N(4) 112.57(14), N(1)−C(19)−N(2) 120.04(15), C(1) ring−NCN 86.9(2), C(10) ring−NCN 50.6(1), C(1) ring−C(10) ring 58.07(5)

Compound **3** represents the first structurally authenticated lithium formamidinate complex that displays neither $\mu_2$:$\eta^2$:$\eta^1$/$\mu_2$:$\eta^1$:$\eta^1$-bridging interactions or an ionic composition. It appears that the added steric buttressing of TMEDA relative to DME imposes enough hindrance to cause **3** to exist as discrete [Li(FMes)(tmeda)] units without intermolecular contacts. Inspite of this, the tetrahedral geometry about the metal centre of **3** is deficient in symmetry [N(1)−Li(1)−N(4) 131.94(15)°, N(2)−Li(1)−N(3) 137.92(15)°, N(3)−Li(1)−N(4) 86.94(12)°]. For example, the N−Li−N planes of the two dinitrogen ligands exist at a dihedral angle of 72.95(6)° to one another, this exacerbates the interaction of the C(11)-bound mesityl ring with the tmeda C(23)-bound $NMe_2$ group. This group counterintuitively leans toward the N(2) side of the formamidinate ligand [N(2)−Li(1)−N(4) 112.57(14)°, N(1)−Li(1)−N(3) 125.52(15)°]. In the absence of an apparent energetic benefit to this, such an anomaly must surely result as a crystal-packing phenomenon. Correspondingly, the disparate dihedral angles of the mesityl rings to the NCN plane [C(1) ring 86.92(15)°, C(11) ring 50.61(14)°] cannot be explained by intramolecular interactions alone. Indeed, one would expect the two mesityl groups to lie orthogonal to the NCN plane, and therefore flat to one another, thereby minimising interaction with the TMEDA ligand. Instead, the mesityl rings exist at a relative torsional angle of 58.07(5)°, which seemingly decries the rationale proposed for the structure exhibited. Reassuringly, the NCN FMes backbone of **3** displays nearly equivalent C−N bond lengths of 1.314(2) and 1.328(2) Å (symptomatic of symmetrical $\eta^2$-chelation) without interaction of C(19) to the metal centre [C(19) projects 0.024 Å above/below the NCN plane). Lastly, the bond lengths N(1)−Li(1) and N(2)−Li(1) [2.036(3) and 2.011(3) Å, respectively) are similar to other symmetrically bonded FMes compounds (**1**, mean: 2.034 Å), whilst the FMes backbone angle of **3** is acute with respect to the $\mu_2$:$\eta^1$:$\eta^1$-bound FMes ligands of **1** [120.04(15)°; **1**: 127.7(3)°], and comparable those of the $\mu_2$:$\eta^2$:$\eta^1$-formamidinate complexes **5** [120.8(3)°][17] and [{Li($\mu_2$:$\eta^2$:$\eta^1$-FTolP)($Et_2O$)}$_2$] [120.0(4)°],[18] and hence closer to the $sp^2$-hybridised ideal of 120°.

## Conclusion

The solid-state structures of **1**−**3** exhibit structural diversity borne out of the rational exchange and substitution of both solvent and aryl substituents. In tandem with archival structural data, we can assert that *N*,*N′*-diarylformamidinates are versatile ligands for lithium, exhibiting an ever increasing number of binding modes and structural motifs. In particular, we have identified the first complexes to display solely $\eta^2$-formamidinate chelation (**2** and **3**), and the first mononuclear Lewis base stabilised group 1 formamidinate to be structurally authenticated (**3**). These studies expand our understanding of the structural ramifications of increased diaryl steric bulk in group 1 systems, which in the extreme negate the interaction of solvent donors, as in the anion of **2**, or frustrate salt formation, as in **1**. In summary, with respect to known FTolP complexes,[17,18] it appears that the presence of *o*-methyl group(s) upon the aryl substituents frustrate, and to a certain extent limit, dimer formation such that $\mu_2$:$\eta^2$:$\eta^1$-formamidinate bridging is not viable (lithium−lithium proximity hindered). This enforces either supplementary solvent coordination or, as seen for **2**, low aggregate lithium−formamidinate anion composition. We are presently extending these studies to ligands of greater steric bulk, e.g. *N*,*N′*-bis(2,6-diisopropylphenyl)formamidine (HFIso), and heavy group 2 and f-block metals. The outcome of these will form the basis of forthcoming publications.

## Experimental Section

**General:** The formamidinate ligand precursors *N*,*N′*-bis(2,4,6-trimethylphenyl)- and *N*,*N′*-bis(*o*-tolyl)formamidine, HFMes and HFTolO, respectively, were synthesised according to published procedures.[18,33] *n*-Butyllithium (1.6 M solution in hexanes) was purchased from Aldrich. 1,2-Dimethoxyethane (DME/dme) and hexane were dried with sodium, freshly distilled from sodium/benzophenone, and freeze-thaw-degassed prior to use. *N*,*N*,*N′*,*N′*-Tetramethylethylenediamine (TMEDA/tmeda) was dried with sodium, freshly distilled from sodium, and freeze-thaw-degassed prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under high-purity argon or dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates with 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 Bruker BZH 300/52 and DPX 300 spectrometers with Varian or Bruker consoles and chemical shifts were referenced to the residual $^1$H or $^{13}$C resonances of the deuteriobenzene solvent employed. Melting points were determined in sealed glass capillaries under argon or dinitrogen and are uncorrected. The high aerobic and moisture sensitivity of compounds **1**−**3**, combined with the facile loss of solvent from both **1** and **2** (as seen for [{Li($\mu_2$:$\eta^2$:$\eta^1$-FTolP)(Et$_2$O)}$_2$], see ref.[18]), frustrated the acquisition of meaningful mass spectrometric and C,H,N microanalytical data. Microanalyses for **1** and **2** were consistently high in carbon and nitrogen, and low in hydrogen, whilst those of **3** were repeatedly low in nitrogen.

**[{Li($\mu_2$:$\eta^1$:$\eta^1$-FMes)(dme)}$_2$].DME (1):** *n*-Butyllithium (0.80 mL, 1.28 mmol) was added dropwise to a stirred ambient-temperature solution of HFMes (0.36 g, 1.28 mmol) in DME (30 mL). Heating of the resultant clear colourless solution to 50 °C for 1 h yielded an opaque-white slurry that was filtered and the filtrate placed at −20 °C. This yielded the title compound as small colourless needles (0.36 g, 67%), m.p. 112 °C (dec.). $^1$H NMR (C$_6$D$_6$, 300 K): $\delta$ = 2.24 (s, 12 H, *p*-CH$_3$), 2.32 (s, 24 H, *o*-CH$_3$), 3.04 (s, 18 H, OCH$_3$), 3.11 (s, 12 H, OCH$_2$), 6.85 (s, 8 H, *m*-H), 7.60 [br. s, 2 H, NC(H)N] ppm. $^{13}$C NMR (C$_6$D$_6$, 300 K): $\delta$ = 18.4 (s, *p*-CH$_3$), 19.6 (s, *o*-CH$_3$), 57.4 (s, OCH$_3$), 70.6 (s, OCH$_2$), 127.7 (s, *m*-C), 128.0, 128.1, 130.7 (s, Ar-C), 157.6 [s, NC(H)N] ppm. IR (Nujol): $\tilde{\nu}$ = 850 m, 872 m, 1022 m, 1090 m, 1124 m, 1146 m, 1209 s, 1246 w, 1294 w, 1564 s, 1614 m, 1639 m cm$^{-1}$.

**[Li(dme)$_3$][Li($\eta^2$-FTolO)$_2$] (2):** *n*-Butyllithium (0.80 mL, 1.28 mmol) was added dropwise to a stirred solution of HFTolO (0.29 g, 1.29 mmol) in DME (30 mL) producing an opaque-yellow solution. Cessation of stirring after 2 h, followed by filtration gave a solution that yielded colourless crystals of the title compound (upon storage at −30 °C) as large solvent-dependent blocks (0.33 g, 71%), m.p. 122 °C (dec.). $^1$H NMR (C$_6$D$_6$, 300 K): $\delta$ = 2.13 (s, 12 H, *o*-CH$_3$), 2.86 (s, 18 H, OCH$_3$), 2.88 (s, 12 H, OCH$_2$), 6.94 (m, 4 H, Ar-H), 7.03 (m, 4 H, Ar-H), 7.15 (m, 8 H, Ar-H), 8.72 [br. s, 2 H, NC(H)N] ppm. $^{13}$C NMR (C$_6$D$_6$, 300 K): $\delta$ = 19.2 (s, *o*-CH$_3$), 58.9 (s, OCH$_3$), 71.1 (s, OCH$_2$), 118.2, 120.1, 127.1, 129.9, 130.6, 150.7 (s, Ar-C), 160.4 [s, NC(H)N] ppm. IR (Nujol): $\tilde{\nu}$ = 811 m, 831 m, 867 m, 921 w, 995 w, 1028 w, 1083 s, 1122 m, 1178 w, 1205 m, 1222 m, 1245 w, 1549 s, 1568 m, 1664 w cm$^{-1}$.

**[Li($\eta^2$-FMes)(tmeda)] (3):** *n*-Butyllithium (1.10 mL, 1.76 mmol) was added dropwise to a stirred solution of HFMes (0.48 g, 1.71 mmol) in hexane (60 mL), instantly yielding a white precipitate. Addition of TMEDA (300 μL, 1.99 mmol) resulted in dissolution of the precipitate, rendering a clear yellow solution that was concentrated in vacuo (ca. 40 mL) and filtered. Placement of the filtrate at −5 °C for one week yielded the title product as a microcrystalline powder and a small quantity of colourless prisms (single product by $^1$H NMR, 0.49 g, 71%), m.p. 145 °C (dec.). $^1$H NMR (C$_6$D$_6$, 300 K): $\delta$ = 1.80 (s, 4 H, NCH$_2$), 1.92 (s, 12 H, NCH$_3$), 2.29 (s, 6 H, *p*-CH$_3$), 2.38 (s, 12 H, *o*-CH$_3$), 6.97 (s, 4 H, *m*-H), 8.02 [br. s, 1 H, NC(H)N] ppm. $^{13}$C NMR (C$_6$D$_6$, 300 K): $\delta$ = 20.0 (s, *o*-CH$_3$), 21.0 (s, *p*-CH$_3$), 45.3 (s, NCH$_3$), 56.5 (s, NCH$_2$), 129.0 (s, *m*-C), 129.4, 131.0, 140.4 (s, Ar-C), 166.1 [br. s, NC(H)N] ppm. IR (Nujol): $\tilde{\nu}$ = 792 m, 851 m, 944 m, 998 m, 1018 m, 1061 w, 1158 m, 1212 m, 1285 s, 1302 m, 1536 s, 1609 w, 1644 w cm$^{-1}$.

**X-ray Crystallography:** Crystalline samples of compounds **1** and **3** were mounted upon glass fibres in silicone grease at −150 °C (123 K). A crystalline sample of **2** was mounted in a 0.5 mm capillary and sealed under argon at ambient temperature. Crystal data for compounds **1** and **3** were obtained using an Enraf−Nonius Kappa CCD. Data for **2** were obtained with a Bruker SMART CCD diffractometer. Data were corrected for absorption using the SADABS program.[34] Structural solution and refinement was carried out using SHELXL-97[35] and SHELXS-97[36] utilising the graphical interface X-Seed.[37] Crystal data and refinement parameters for all complexes are compiled in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-186011 (**1**), -186013 (**2**) and -186012 (**3**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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