Structural Studies of *N*,*N*′-Di(*ortho*-fluorophenyl)formamidine Group 1 Metallation

Marcus L. Cole,[a] David J. Evans,[a] Peter C. Junk,*[a] and Matthew K. Smith[a, b]

Abstract: The treatment of *N*,*N*′-di(*ortho*-fluorophenyl)formamidine (HFPhF) in tetrahydrofuran with equimolar amounts of *n*-butyllithium, sodium bis(trimethylsilyl)amide or potassium bis(trimethylsilyl)amide affords the colourless crystalline formamidinate complexes [Li(FPhF)(thf)] (**1**), [Na(FPhF)(thf)] (**2**) and [K(FPhF)] (**5**). Low-temperature preparation of **2** in diethyl ether yields the Et_2O adduct [Na(FPhF)(Et_2O)] (**3**). At ambient temperature the sodium fluoride inclusion complex [Na_3(FPhF)$_3$(Et_2O)(NaF)] (**4**) is also formed. Spectroscopic (^{1}H, ^{13}C and ^{19}F{^{1}H} NMR) data for **1**–**5**, microanalytical analyses for compounds **1**, **2** and **5** and X-ray structure determinations for **1**, **3**–**5** confirm the formulae of these species. In the solid-state, **1** and **3** possess a dimeric nature in which the formamidinate ligands coordinate through μ_2:η^2:η^1 (**1**) and μ_2:η^2:η^2 (**3**) binding modes. These are enabled by partial *ortho*-fluoro donation. Compound **4**, which is also dimeric, contains two trisodium tris(formamidinate) units that comprise μ_2:η^2:η^2-FPhF ligands, a bridging diethyl ether moiety and an unprecedented μ_3:η^2:η^2:η^2-formamidinate donor. Together, these trinuclear units encapsulate two sodium fluoride units by η^2-*N*,*N*-formamidinate chelation of the sodium cations (thereby creating further μ_3:η^2:η^2:η^2-bound formamidinates) and fluoride–sodium interactions. Compound **5** extends the coordinative versatility of FPhF to μ_2:η^4:η^3 coordination by the generation of $K_2(\mu_2$:η^4:η^3-FPhF$)_2$ units that exhibit η^2-arene interactions. Macromolecularly, the overlaying of these units affords a polymeric solvent-free structure that incites coordination of the FPhF ligands to metal atoms above and below the K_2(FPhF)$_2$ plane. Overall, this generates a remarkable μ_4:η^4:η^3:η^2:η^1-amidinate binding mode that incorporates both bridging and terminal fluorine donors. Compounds **1**–**5** are the first non-chromium complexes of *N*,*N*′-di(*ortho*-fluorophenyl)formamidinate.

Keywords: alkali metals · amidinates · coordination modes · inclusion compounds · N ligands

Introduction

The chemistry of amidinate ligands of the type [$R^1NC(R^2)NR^1$]$^-$ includes elements spanning the periodic table. Historically, most interest has centred upon the use of Group 1 amidinates, particularly those of lithium, as metathesis reagents in the preparation of "paddle-wheel" dinuclear transition metal species, general formula [M_2(amidinate)$_4$]$^{0,+1\text{ or }+2}$,[1] wherein close metal–metal proximity incites fascinating magnetic and electronic properties. Of these, the significant works of Cotton and co-workers have made extensive use of *N*,*N*′-di(aryl)formamidinates (R^2 = H).[2–6] These possess greater conformational dexterity than related alkyl/aryl/amido-substituted amidinates/guanidinates courtesy of an unencumbered NCN backbone.[7]

In spite of the emphasis placed upon Group 1 formamidinates (cf. the above preparations), their structural study has been somewhat overlooked. Indeed, prior to a report by Cotton and Murillo in 1997[8] no s-block formamidinate complexes had been characterised in the solid state. The rationale put forward for this was the facility by which donor solvent was lost, thereby frustrating crystallographic characterisation. Conversely, several benzamidinate (R^2 = Ph) complexes of lithium were structurally authenticated prior to 1997.[9–11] Without exception, these species included donors of recognised strong chelation or donation.

Recently, the focus of amidinate research has swayed from the dinuclear transition metal species of the preceding decades toward Group 13 metal catalytic studies popularised,[12–14] amongst others, by Jordan et al.[15–17] To compliment these, the amidinate chemistries of Groups 2 and 14[18–42] have also received attention in an effort to exploit an untapped research area. In stark contrast, the study of Group 1 amidinate chemistry, particularly formamidinate, has remained scarce.[8, 43–50] The groups of both Lappert[51–59] and Arnold[60–64] have done most to address this by advancing the chemistry of benzamidinates and guanidinates (R^2 = NR_2). However, given the considerable structural diversity exhib-

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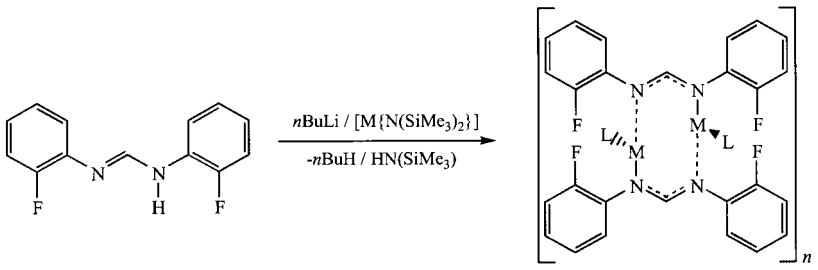
ited by transition metal amidinate species, which in short encompasses η^1-monodentate, for example [Pt{2-6-(CH_2N{CH_3}$_2$)$_2$$C_6H_3$}{(4-$CH_3$-$C_6H_4$)NC(H)N(4-$CH_3$-$C_6H_4$)}];[65] η^1:η^1-symmetrical diazaallyl, for example [{Pt((C_6H_5)NC(C_6H_5)-N(C_6H_5))}$_2$];[66] η^1:η^1-unsymmetrical diazaallyl, for example, [Ta(CH_3)Cl_2{(C_6H_{11})NC(CH_3)N(C_6H_{11})}$_2$][67] and μ_2:η^1:η^1-amidinate, for example, homometallic [Mo_2{(C_6H_5)NC(C_6H_5)-N(C_6H_5)}$_4$][68] or heterobimetallic [Pt{2-6-(CH_2N{CH_3}$_2$)$_2$-C_6H_3}Hg{μ-{(4-CH_3-C_6H_4)NC(H)N(*i*Pr)}(Br)(Cl)],[69] we believe the full structural versatility of s-block metallated amidinates has not been comprehensively researched. An example of this versatility can be seen in acetamidinate and benzamidinate complexes of pentamethylcyclopentadienyl ruthenium, which have generated the first examples of recognised η^3-diazaallyl coordination (NCN fragment bound "near" side-on to maximise diazaallyl π-donation).[70, 71]

The unusual μ_2:η^2:η^1-binding mode of *N*,*N*′-di(*para*-tolyl)formamidinate (FTolP) in the first lithium formamidinate complex [{Li(FTolP)(Et_2O)}$_2$],[8] which has no transition metal equivalent, and the highly ionic nature of Group 1 amides suggest the chemistry of Group 1 formamidinates may possess structural novelty beyond that of d-block systems.[72] To assess this, we have embarked upon a detailed crystallographic study of both Group 1 and 2 formamidinate complexes.[73–78] Thus far, employing the ligands FTolP, FTolO (*N*,*N*′-di(*ortho*-tolyl)formamidinate), and FMes (*N*,*N*′-di-(2,4,6-trimethylphenyl)formamidinate), under different solvent conditions, this has provided rich structural diversity within each element class, for example [{Li(μ_2:η^1:η^1-FMes)-(dme)}$_2$][76] (DME = 1,2-dimethoxyethane) and [Li_2(μ_2:η^1:η^1-FTolP)$_2$(μ_2:η^2:η^2-FTolP)(thf)$_2$(μ_2-thf)];[75] [Na_3(μ_3:η^2:η^1:η^1-FTolP)$_2$(μ_2:η^2:η^2-FTolP)(thf)$_4$][75] and [{Na(μ_2:η^2:η^1-FTolP)(dme)}$_2$]);[75] and [{K_2(μ_2:η^2:η^2-FTolP)$_2$(μ_2-thf)$_3$}$_\infty$][77] and [K{(η^6-Mes)NC(H)-N(Mes)}{(η^6-Mes)NC(H)NH(Mes)][73] (Mes = 2,4,6-trimethylphenyl). To further the binding remit of formamidinate species and utilise the highly electropositive nature of the lighter Group 1 elements, we have now chosen to investigate the Group 1 metallation chemistry of *N*,*N*′-di(*ortho*-fluorophenyl)formamidine (HFPhF). In exploiting the established precedent for fluorinated-arene fluoro coordination to proximal metal centres,[79] we hope that coordination of FPhF to lithium, sodium and potassium will frustrate the inclusion of solvent donors and elaborate upon an ever-growing number of novel amidinate binding modes.

Herein, the results of this study are reported. In all instances fluoro coordination is prevalent amongst the structural make up of Group 1 FPhF species. As hoped, this limits solvent coordination and encourages greater formamidinate–metal interaction. In the extreme, such interactions afford the solvent-free species [{K(μ_4:η^4:η^3:η^2:η^1-FPhF)$_\infty$}] (**5**), which, in addition to potassium–fluorine and –arene interactions, exhibits a tetranuclear μ_4:η^2:η^1:η^1:η^1-NCN bound amidinate. This binding mode is unique to compound **5** and represents the greatest amidinate–metal interaction hitherto reported.[80, 81]

Results and Discussion

Treatment of tetrahydrofuran solutions of HFPhF with equimolar amounts of *n*-butyllithium, sodium bis(trimethylsilyl)amide or potassium bis(trimethylsilyl)amide results in clean deprotonation of the formamidine amino group (Scheme 1) yielding highly air- and moisture- sensitive crystalline products that characterise as [Li(FPhF)(thf)] (**1**), [Na(FPhF)(thf)] (**2**) and [K(FPhF)] (**5**) by ^{1}H NMR spectroscopy (C_6D_6, non-donating solvent used to preclude further solvent donation) and C, H, N microanalyses. Spectroscopy confirms deprotonation due to the absence of resonances and



Scheme 1. Reagents and conditions: **1**: *n*BuLi, L = THF, *n* = 1; **2**: M = Na, L = THF, *n* = 1; **3**: M = Na, L = Et_2O, *n* = 1; **5**: M = K, L = no solvent, *n* = ∞.

stretches attributable to the N–H moiety of HFPhF. These occur at $\delta = 5.87$ ppm and $\tilde{\nu} = 3015$ cm^{-1} (^{1}H NMR N(H) resonance signal and FTIR N–H stretch, respectively).[82] Furthermore, the delocalisation of π electrons across the NCN backbone inherent of deprotonation, shields the methyne proton (NC(H)N), shifting backbone HFPhF resonances at $\delta = 7.55$ and 147.2 ppm (^{1}H and ^{13}C NMR spectroscopy, respectively)[82] to $\delta = 8.07$ and 158.4 (**1**), 8.65 and 142.7 (**2**), and 8.58 and 161.4 ppm (**5**). The placement of these resonance signals complies with those of Group 1 FTolP-tetrahydrofuran species ($\delta \approx 8.60$ and 160 ppm, respectively)[75, 77] and is radically different to those of the unusual η^6:η^1-chelated formamidinate in [K{(η^6-Mes)NC(H)N(Mes)}{(η^6-Mes)NC(H)NH(Mes)] ($\delta = 9.13$ and 182.5 ppm [D_8]THF).[73] This suggests that, unlike [K{(η^6-Mes)NC(H)N(Mes)}{(η^6-Mes)NC(H)NH(Mes)], compounds **1**, **2** and **5** do not exhibit aryl–metal coordination in solution. Indeed, the presence of orthodox non-fluxional aryl environments for all three species, as indicated by ^{1}H NMR spectroscopy, suggests the FPhF ligands of **1**, **2** and **5** bind the metal centres by conventional NCN binding modes. This may or may not be augmented by fluorine donation from the *ortho*-fluoro groups as all three species exhibit sharp singular ^{19}F{^{1}H} NMR resonance signals (–129.7 (HFPhF), –126.7 (**1**), –135.9 (**2**), –130.5 ppm (**5**)). To discover whether these symmetrical coordination modes are an artefact of rapid solution-state fluxional processes, single crystals of **1**, **5** and [Na(FPhF)(Et_2O)] (**3**) were grown from their respective reaction media and X-ray structure determinations undertaken. Compound **3** was prepared as all attempts to grow suitable crystals of **2** (for spectroscopic data, see the Experimental Section) failed. Unlike **2**, but like [{Li((μ_2:η^2:η^1-FTolP)(Et_2O)}$_2$],[8] the inclusion of diethyl ether in **3** (the preparation medium employed, see Scheme 1) furnishes **3** with extreme solvent dependency

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(loss of crystallinity over a period of seconds when removed from mother liquor), this frustrated the acquisition of meaningful microanalytical data for **3** and resulted in an inferior thermal stability compared to **2** (**3**: 238 °C (decomp); **2**: 265 °C (decomp); **1**: 121 °C; **5**: 234 °C). The molecular structures of **1**, **3** and **5** can be seen in Figures 1, 2, 5 and 6, respectively (POV-RAY illustrations, 30% thermal ellipsoids); selected bond lengths and angles are given in the captions to the figures. X-ray diffraction data for all complexes are listed in Table 1.

Compound **1** crystallises in the monoclinic space group $P2_1/n$ with half a dimeric $[\{Li(\mu_2{:}\eta^2{:}\eta^1\text{-FPhF})(thf)\}_2]$ unit in the asymmetric unit. The *exo*-NCN chelation of FPhF incurred by fluorine donation (F(2), see Figure 1) precludes the incorporation of more than one solvent donor (as exhibited by $[Li_2(\mu_2{:}\eta^1{:}\eta^1\text{-FTolP})_2(thf)_2(\mu_2\text{-thf})]$)[75] or greater than η^1-NCN formamidinate coordination to each metal centre (as exhibited by $[\{Li(\mu_2{:}\eta^2{:}\eta^1\text{-FTolP})_2(Et_2O)\}_2]$).[8] This induces a significantly large Li···Li distance of 3.234(8) Å, the aforementioned FTolP species exhibiting analogous distances of 2.794(14) Å[75] and 2.61(2) Å.[8] Furthermore, as a consequence of nitrogen/fluorine chelation to each lithium centre, of which the Li–F bonds possess a length of 2.114(4) Å (mean Li–F bond length structurally characterized 1.970 Å),[43] the lithium atoms reside in highly distorted tetrahedral environments (N(1)-Li(1)-N(1)# 125.3(2)°, O(1)-Li(1)-F(2) 105.9(2)°). This is similar to the lithium atoms of $[Li_2(\mu_2{:}\eta^1{:}\eta^1\text{-FTolP})_2(thf)_2(\mu_2\text{-thf})]$ (O_{THF}-Li-$O_{\mu\text{-THF}}$ 102.8(4)°, N-Li-O_{THF} 113.8(3)°) and $[\{Li((\mu_2{:}\eta^2{:}\eta^1\text{-FTolP})_2(Et_2O)\}_2]$ (O_{Et2O}-Li-Nη^1 121.6(4)°, Nη^1-Li-Nη^2 120.0(4)°),[8] whilst the Li–O_{THF} distance of **1** (1.944(4) Å) is comparable to that of the tetrahydrofuran ligands in $[\{Li(2\text{-}AsMe_2\text{-}C_6H_4NH)(thf)_2\}_2]$ (1.94(2) Å and 1.96(2) Å, lithium centres also four coordinate).[83] Within the formamidinate ligand, the bond lengths in the carbon–nitrogen backbone of **1** suggest delocalisation of the anionic charge across the NC(H)N unit (1.318(3) Å and 1.343(3) Å; variation 0.025 Å, those of $[\{HFTolP\}_2]$; 1.340(2) Å and 1.414(2) Å, suggestive of discrete single and double C–N bonds).[75] However, as a consequence of $\mu_2{:}\eta^2{:}\eta^1$ binding, the NCN backbone of the FPhF ligand exists at an obtuse angle of 122.0(2)°. This is closed with respect to the protonated ligand (122.45(11)°),[82] and intermediate to those of $[Li_2((\mu_2{:}\eta^1{:}\eta^1\text{-FTolP})_2(thf)_2(\mu_2\text{-thf})]$ (123.3(4)°)[75] and $[\{Li((\mu_2{:}\eta^2{:}\eta^1\text{-FTolP})_2(Et_2O)\}_2]$ (120.0(4)°),[8] presumably because the conformational NCN strain exhibited by **1** lies in between that of pure $\mu_2{:}\eta^1{:}\eta^1$ and $\mu_2{:}\eta^2{:}\eta^1$ coordination. The lack of symmetry displayed by the binding of FPhF within **1** is alluded to by the differing carbon–fluorine bond lengths for each aryl group, F(1)–C(2) 1.364(3), F(2)–C(8) 1.393(3) Å, that of the donor group being extended as a result of donation of fluorine electron density

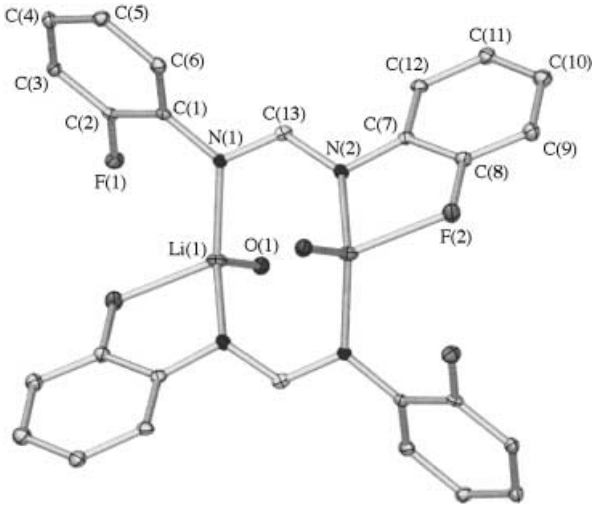

Figure 1. Molecular structure of $[\{Li(\mu_2{:}\eta^2{:}\eta^1\text{-FPhF})(thf)\}_2]$ (**1**). All hydrogen atoms and tetrahydrofuran C_4H_8 tethers omitted for clarity. Relevant bond lengths [Å] and angles [°]: Li(1)–N(1) 2.014(4), Li(1)#–N(2) 1.989(4), Li(1)#–F(2) 2.114(4), Li(1)–O(1) 1.944(4), N(1)–C(13) 1.318(3), N(2)–C(13) 1.343(3), C(2)–F(1) 1.364(3), C(8)–F(2) 1.393(3); Li(1)-N(1)-C(13) 116.10(19), Li(1)#-N(2)-C(13) 124.5(2), N(1)-C(13)-N(2) 122.0(2), C(1)-N(1)-C(13) 115.18(19), C(7)-N(2)-C(13) 115.9(2), C(8)-F(2)-Li(1)# 110.52(17), N(1)-Li(1)-N(2)# 125.3(2), N(1)-Li(1)-O(1) 107.4(2), N(1)-Li(1)-F(2)# 114.7(2), O(1)-Li(1)-N(2)# 118.4(2), O(1)-Li(1)-F(2)# 105.86(19), F(2)#-Li(1)-N(2)# 80.83(16). Symmetry transformation used to generate # atoms: $-x+2, -y+2, -z$.

Table 1. Summary of crystal data for compounds **1** and **3**–**5**.

	1	**3**	**4**	**5**
formula	$C_{17}H_{174}Li_1N_2O_1F_2$	$C_{17}H_{19}Na_1N_2O_1F_2$	$C_{86}H_{74}Na_8N_{12}O_2F_{14}$	$C_{13}H_9K_1N_2F_2$
M_w	310.27	328.33	1757.49	270.32
T[K]	123(2)	123(2)	123(2)	123(2)
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a[Å]	9.5714(19)	7.9919(16)	21.870(4)	3.9708(8)
b[Å]	7.6956(15)	15.671(3)	17.942(4)	11.558(2)
c[Å]	21.129(4)	13.450(3)	21.800(4)	25.035(5)
β[°]	99.50(3)	94.92(3)	94.28(3)	91.99(3)
V[Å^3]	1535.0(5)	1678.3(6)	8530(3)	1148.3(4)
Z	4	4	4	4
ρ_{calcd}[g cm^{-3}]	1.343	1.299	1.369	1.564
μ[mm^{-1}]	0.100	0.119	0.140	0.469
reflns collected	15665	12301	81899	13453
reflns observed	3806	4077	20919	2812
parameters varied	276	210	1103	164
R(int)	0.1006	0.0664	0.1077	0.0722
R_1	0.0575	0.0660	0.0533	0.0984
wR_2	0.1654	0.1718	0.1036	0.2581

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and the minute closing of the *ipso* C-C-F angle of F(2) with respect to the aryl group of F(1) (116.6(2)° and 117.6(2)°, respectively). This has implications for the Li–N bonds adjacent to each group, wherein that of N(1) is slightly longer (2.014(4) Å) than that of N(2) (1.989(4) Å), the discrepancy arising from greater ligand N–Li contact enforced by Li···F contact. Irrespective of this, these Li–N bond lengths are shorter than the mean of those structurally authenticated (mean Li–N bond length of four-coordinate lithium amides 2.096 Å).[43]

Similar to **1**, compound **3** crystallises in a monoclinic space group ($P2_1/c$) with half a dinuclear [{Na(μ_2:η^2:η^2-FPhF)(Et$_2$O)}$_2$] unit in the asymmetric unit (Figure 2). The increase

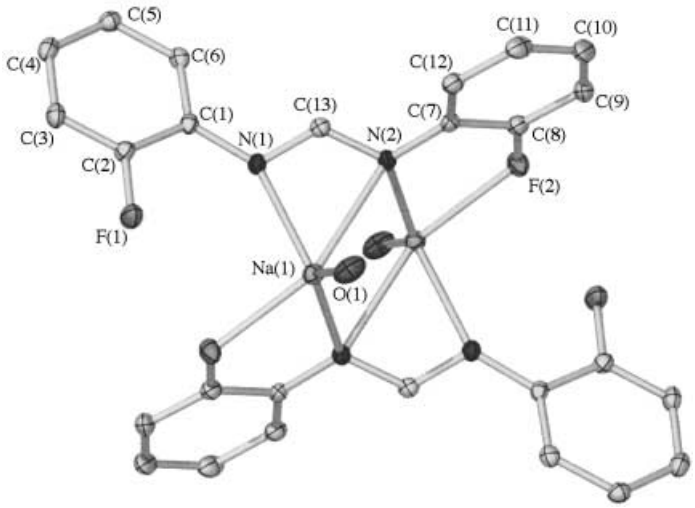

Figure 2. Molecular structure of [{Na(μ_2:η^2:η^2-FPhF)(Et$_2$O)}$_2$] (**3**). All hydrogen atoms and diethyl ether ethyl groups omitted for clarity. Relevant bond lengths [Å] and angles [°]: Na(1)–N(1) 2.350(2), Na(1)–N(2) 2.580(2), Na(1)#–N(2) 2.424(2), Na(1)#–F(2) 2.345(2), Na(1)–O(1) 2.344(2), N(1)–C(13) 1.300(3), N(2)–C(13) 1.337(3), C(2)–F(1) 1.363(3), C(8)–F(2) 1.371(3); Na(1)-N(1)-C(13) 92.76(16), Na(1)-N(2)-C(13) 82.17(15), Na(1)#-N(2)-C(13) 123.25(18), N(1)-C(13)-N(2) 121.8(2), C(1)-N(1)-C(13) 117.9(2), C(7)-N(2)-C(13) 116.6(2), C(8)-F(2)-Na(1)# 117.94(15), N(1)-Na(1)-N(2) 55.50(7), N(1)-Na(1)-N(2)# 111.15(9), N(1)-Na(1)-O(1) 112.92(8), N(1)-Na(1)-F(2)# 96.68(8), Na(2)-Na(1)-F(2)# 144.11(8), N(2)-Na(1)-N(2)# 97.99(8), O(1)-Na(1)-N(2)# 134.64(8), O(1)-Na(1)-F(2)# 114.99(9), F(2)#-Na(1)-N(2)# 69.23(7). Symmetry transformation used to generate # atoms: $-x+1, -y, -z$.

in metallic radii from **1** to **3** (Li 0.60, Na 1.00 Å)[84] facilitates an η^2-chelate interaction to each metal centre. Discounting fluorine–sodium interactions, this structural motif is similar to that of the FTolP ligands within [{Na(μ_2:η^2:η^1-FTolP)(DME)}$_2$].[75] Similar to this species, the sodium atoms of **3** reside in a distorted trigonal-bipyramidal environment (F(2)-Na(1)-N(2) 144.11(8)°, O(1)-Na(1)-N(1) 112.92(8)°) with a fluoro group (F(2)) taking the place of one ethereal oxygen donor (cf. chelating donor in [{Na(μ_2:η^2:η^1-FTolP)(dme)}$_2$]).[75] As per **1**, this creates a distortion of the *N*,*N*′-di(aryl)formamidinate frame leading to disparate sodium–nitrogen bond lengths of 2.350(2) and 2.424(2) Å (*intra*-$N_4C_2Na_2$ metallocycle Na–N bond length 2.580(2) Å), meanwhile η^2 chelation has little effect upon the NCN backbone angle (**1**: 121.8(2)°; 122.0(2)° **3**) and renders N(2) tetrahedral (distorted geometry; Na(1)-N(2)-N(1)# 82.01(8), C(7)-N(2)-Na(1) 133.16(17). One ramification of fluorine···sodium contact is lesser metal–metal proximity for **3** than [{Na(μ_2:η^2:η^1-FTolP)(dme)}$_2$][75] resulting from *exo*-NCN ligand–metal interaction (3.285(2) and 3.080(2) Å, respectively). This constricts the carbon-nitrogen-*ipso*-carbon angles (at F(2) 117.9(2)° versus angle at F(1) 116.2(2)°); however, with respect to the NCN backbone, surprisingly this results in little perturbation of the NCN dihedral angles between the F-coordinated aromatic groups and the non-F-coordinated aromatic groups, unlike **1** (**3**; C(1)–C(6) ring plane to the NCN plane 44.5(2)°, C(7)–C(12) ring plane to the NCN plane 48.6(3)°, **1**; C(1)–C(6) ring plane to the NCN plane 56.2(2)°, C(7)–C(12) ring plane to the NCN plane 41.2(2)°). The Na–F bonds responsible for decreased metal–metal distances (see above) have a length of 2.345(3) Å (mean of those structurally characterised; 2.438,[43] C(2)–F(1) 1.363(3), C(8)–F(2) 1.371(3) Å). Fluorine coordination has a moderate effect upon the typically symmetrical formamidinate carbon–nitrogen bond lengths, those of the NCN unit are 1.300(3) and 1.337(3) Å. Meanwhile, the sodium to ethereal oxygen distance of 2.344(2) Å is similar to those observed in [{Na{(SiMe$_3$)NC(C$_6$H$_5$)N(SiMe$_3$)}(Et$_2$O)}$_2$] (mean 2.329 Å).[48] Overall, the metal–oxygen/nitrogen lengths of **3** are shorter than those structurally authenticated (CCSD: Na–O 2.450, Na–N$_{amido}$ 2.442 Å, see Figure 2 for Na–N bonds of **3**).[43]

During the preparation of **3** at ambient temperature, a second crystalline product [{Na$_3$(μ_3:η^2:η^2:η^2-FPhF)$_3$(μ_2-Et$_2$O)(NaF)}$_2$] (**4**) was isolated by fractional crystallisation (Figures 3 and 4, see the Experimental Section for spectroscopic data). The composition of compound **4** presumably results from a lack of reaction control during the diethyl ether solvated deprotonation of HFPhF by sodium bis(trimethylsilyl)amide. We speculate that this manifests itself as metathesis at the *ortho*-fluorophenyl positions of **3** (rather than metathesis with unreacted HFPhF), thereby eliminating sodium fluoride in situ. The subsequent trapping of sodium fluoride by [{Na(FPhF)}$_n$(Et$_2$O)$_m$] renders **4** ($n=3$, $m=1$), suggesting that the solution-state composition of **3** differs from that observed in the solid state. Preparation of **3** at decreased temperatures (−50 °C) inhibits the formation of **4**, as evidenced by the absence of resonance signals at $\delta=7.08$ and 8.49 ppm in ^{1}H NMR spectra of the bulk product (C_6D_6). These resonance signals, indicative of complex **4** (see the Experimental Section), repeatedly appear in bulk samples of **3** prepared at ambient temperature; however, no analogous products are identified in the bulk reaction material of preparations of **1**, **2** and **5** in tetrahydrofuran. Why this should be is largely a point of conjecture; however, complex **4** can be intentionally synthesised in high yield (≈80% by ^{1}H NMR) by the treatment of HFPhF with 9/7 equivalents of sodium bis(trimethylsilyl)amide. This reaction presumably proceeds according to the path described in Scheme 2. Attempts to isolate the hypothetical sodium *N*,*N*′-di(*ortho*-bis(trimethylsilyl)aminophenyl)formamidinate by-product of this reaction have proved fruitless probably due to increased solubility. However, in view of the accepted stronger donor characteristics of THF compared to diethyl ether, we believe the absence of a **4**-like species in the syntheses of **1**, **2** and **5** suggests that, whilst diethyl ether donation is relatively labile,

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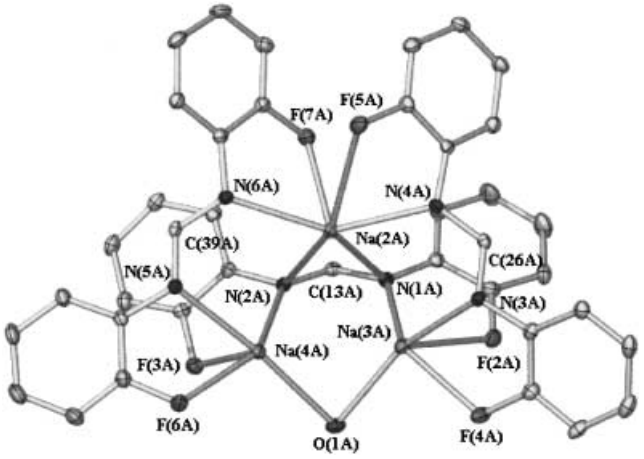


Figure 3. Molecular structure of one of the trinuclear $[\{Na_3(\mu_2{:}\eta^2{:}\eta^2\text{-}FPhF)_2(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FPhF)((\mu_2\text{-}Et_2O)\}]$ capping units within the asymmetric unit of **4**. All hydrogen atoms and diethyl ether ethyl groups omitted for clarity. Relevant bond lengths [Å] and angles [°]: N(1A)–Na(2A) 2.6812(19), N(2A)–Na(2A) 2.569(2), N(1A)–Na(3A) 2.429(2), N(2A)–Na(4A) 2.455(2), F(2A)–Na(3A) 2.6096(16), F(3A)–Na(4A) 2.4034(16), F(2A)–C(2A) 1.374(3), F(3A)–C(8A) 1.384(3), N(4A)–Na(2A) 2.506(2), N(3A)–Na(3A) 2.372(2), F(4A)–Na(3A) 2.4302(17), F(5A)–Na(2A) 2.9312(17), F(4A)–C(15A) 1.377(3), F(5A)–C(21A) 1.374(3), N(5A)–Na(4A) 2.485(2), N(6A)–Na(2A) 2.495(2), F(6A)–Na(4A) 2.4113(17), F(7A)–Na(2A) 2.4353(16), F(6A)–C(28A) 1.380(3), F(7A)–C(34A) 1.387(2), Na(3A)–O(1A) 2.438(2), Na(4A)–O(1A) 2.5306(18), N(1A)–C(13A) 1.321(3), N(2A)–C(13A) 1.309(3), N(3A)–C(26A) 1.323(3), N(4A)–C(26A) 1.327(3), N(5A)–C(39A) 1.323(3), N(6A)–C(39A) 1.324(3); Na(3A)-O(1A)-Na(4A) 80.71(5), N(1A)-C(13A)-N(2A) 121.4(2), N(3A)-C(26A)-N(4A) 121.4(2), N(5A)-C(39A)-N(6A) 121.1(2), N(4A)-Na(2A)-F(5A) 58.06(5), N(6A)-Na(2A)-F(7A) 67.42(6), N(1A)-Na(2)-N(2A) 51.75(6), N(1A)-Na(3A)-F(2A) 65.26(6), N(1A)-Na(3A)-O(1A) 89.40(6), N(3A)-Na(3A)-F(4A) 68.42(6), N(2A)-Na(4A)-O(1A) 90.67(6), N(5A)-Na(4A)-F(6A) 65.92(6), N(2A)-Na(4A)-F(3A) 67.60(6).

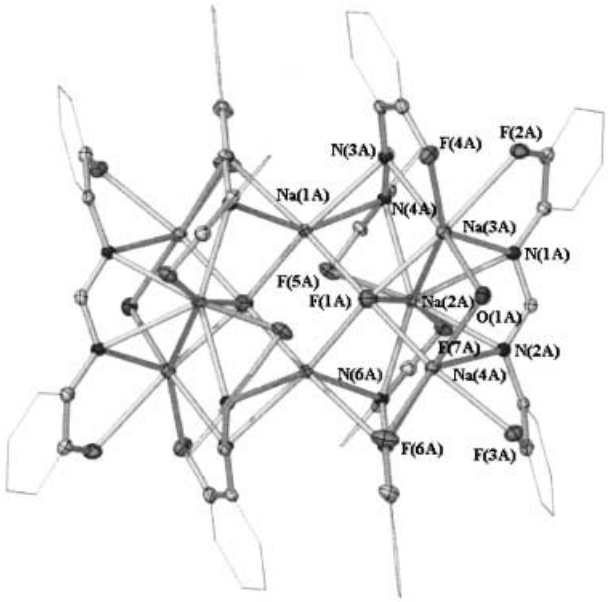
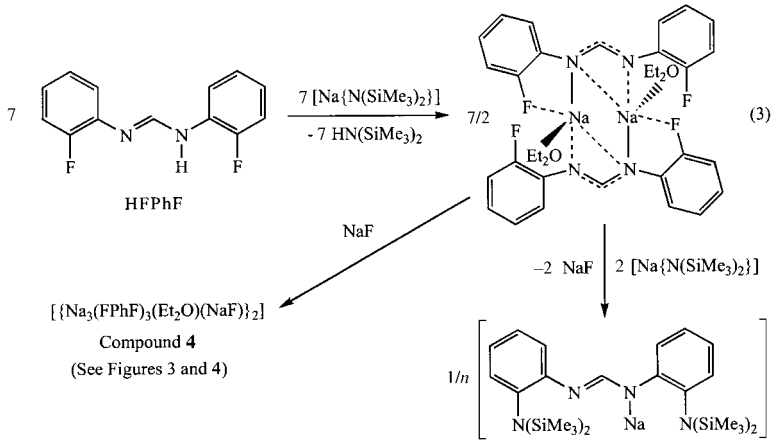


Figure 4. Molecular structure of one of the dimeric units of $[\{Na_3(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FPhF)_3(\mu_2\text{-}Et_2O)(NaF)\}_2]$ in **4**. All hydrogen atoms and diethyl ether ethyl groups omitted for clarity. Relevant bond lengths [Å] and angles [°] not listed in Figure 3: Na(1A)–F(1A) 2.3710(18), Na(1A)–F(1A)# 2.3877(16), Na(1A)–N(3A) 2.5828(19), Na(1A)–N(5A)# 2.509(2), Na(1A)–N(4A) 2.509(2), Na(1A)–N(6A)# 2.582(2), F(1A)–Na(2A) 2.3010(18), F(1A)–Na(3A) 2.3942(16), F(1A)–Na(4A) 2.2968(18); N(5A)#-Na(1A)-F(1A) 160.46(7), N(4A)-Na(1A)-N(6A)# 147.98(7), N(3A)-Na(1)-F(1A)# 168.14(7), F(1A)-Na(1A)-F(1A)# 91.89(5), N(3A)-Na(1A)-F(5A)# 94.42(6), Na(2A)-F(1A)-Na(3A) 81.67(6), Na(2A)-F(1A)-Na(4A) 87.64(6), Na(2A)-F(1A)-Na(1A) 84.66(6), Na(2A)-F(1A)-Na(1A)# 85.64(6), Na(1A)-F(1A)-Na(4A) 172.00(8), Na(3A)-F(1A)-Na(1A)# 166.77(8), Na(3A)-F(1A)-Na(4A) 86.59(5), Na(1A)-F(1A)-Na(1A)# 88.11(5). Symmetry transformation used to generate # atoms: $-x+1, -y+2, -z$.

the robust coordination of THF inhibits the metathesis reaction that leads to **4**.

Compound **4** crystallises in the monoclinic space group $P2_1/c$ with two unique half molecules of $[\{Na_3(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FPhF)_3(\mu_2\text{-}Et_2O)(NaF)\}_2]$ in the asymmetric unit. On account of the similar metrical parameters of both molecules, for which the remaining halves are formed by crystallographic inversion, only molecule "A" is discussed here. As depicted in Figures 3 and 4, the molecular structure of compound **4** consists of two trisodium tris(formamidinate) units that comprise $\mu_2{:}\eta^2{:}\eta^2$-FPhF ligands, a bridging diethyl ether moiety and an unprecedented $\mu_3{:}\eta^2{:}\eta^2{:}\eta^2$-formamidinate donor. These encapsulate two sodium fluoride fragments by η^2-*N*,*N*-formamidinate chelation of the sodium cations by the $\mu_2{:}\eta^2{:}\eta^2$-ligands, thereby creating a further unique $\mu_3{:}\eta^2{:}\eta^2{:}\eta^2$-formamidinate binding mode, and sodium–fluoride interactions. Ignoring fluorine–metal coordination, the two distinct sets of formamidinate ligands display $\mu_3{:}\eta^2{:}\eta^1{:}\eta^1$-amidinate bonding similar to that of $[Na_3(FTolP)_3(thf)_4]$,[75] wherein two $\eta^2{:}\eta^1{:}\eta^1$-FTolP ligands coordinate a trisodium moiety in tandem with a singular $\mu_2{:}\eta^2{:}\eta^2$-FTolP ligand (N-Na-N bite and NCN angles, μ_3-FTolP; mean 51.2° and mean 121.7°, $\mu_2{:}\eta^2{:}\eta^2$-FTolP; mean 52.2° and 121.9(11)°).[75] This motif renders the NCN-chelate bite angles to Na(2A), Na(1A) and Na(1A)# small (N(1A)-Na(2A)-N(2A)



Scheme 2. Generation of $[\{Na_3(\mu_3{:}\eta^2{:}\eta^2{:}\eta^2\text{-}FPhF)_3(\mu_2\text{-}Et_2O)(NaF)\}_2]$ (**4**) from addition of excess sodium bis(trimethylsilyl)amide.

51.75(6)°, N(3A)-Na(1A)-N(4A) 53.97(6)°, N(5A)-Na(1A)#-N(6A) 53.83(6)°) when compared to those of [Na{(2,6-*i*Pr-C_6H_3)NC(H)N(2,6-*i*Pr-C_6H_3)}$(thf)_3$] (56.54(7)°)[82] and **3** (55.50(7)°)[73] because of depreciated ligand–metal contact. Unsurprisingly, this and the congested nature of **4** afford extended sodium–nitrogen contacts relative to other less-congested sodium amidinate species (mean 2.50 Å, mean **3** 2.45 Å,[73] mean of those in trimeric tris(amidinate) [{Na((C$_6$H$_{11}$)NC{N(SiMe$_3$)$_2$}N(C$_6$H$_{11}$))}$_3$]·C$_6$H$_5$CH$_3$ 2.49 Å).[61] It appears unlikely that this extension results from fluorine electron withdrawal from the NCN-formamidinate subunit. This hypothesis is supported by the short nature of the M–N bonds of compound **4**, and also those of **1**, **3** and **5** (see below), relative to Group 1 metal amide bonds in the structural archive, and the similar length of the M–N bonds in compounds **1**, **3**–**5** to the mean M–N lengths of relevant Group 1 FTolP species [$Li_2(\mu_2{:}\eta^1{:}\eta^1$-FTolP)$_2(\mu$-thf)(thf)$_2$] (2.028 Å),[75] [$Na_2(\mu_2{:}\eta^2{:}\eta^1$-FTolP)$_2(dme)_2$] (2.481 Å)[75] and [K($\eta^2$-FTolP)([18]crown-6)] (2.876 Å).[77] Furthermore, the symmetrical formamidinate environments of **4** incur backbone C–N bond lengths that describe complete delocalisation of the anionic charge across the backbone, the variation within each ligand being 0.012, 0.004 and 0.001 Å ([{HFTolP}$_2$], mean C–N 1.409, C=N 1.347 Å).[75] The trinuclear sodium fluoride 'trapping' moieties of **4** are noteworthy in that they represent the fourth trisodium tris(amidinate) unit structurally authenticated, the metal–amidinate "trimer" motif appearing preferential to sodium.[52, 61, 75] In addition, although species containing bridging THF moieties are somewhat common,[85] the diethyl ether ligands of **4** are the only reported example of a bridging Et_2O (Na(3A)–O(1A) 2.438(2), Na(4A)–O(1A) 2.5306(18) Å; mean structurally characterised Na–O distance; 2.450 Å).[43] Finally, coordination of the sodium and fluorine atoms of NaF by these trinuclear "*pseudo*-ligand" units present sodium–fluoride and nitrogen–sodium bond lengths in the ranges 2.297–2.394(2) and 2.509(2)–2.583(2) Å. These are shorter and longer, respectively, relative to those in the Cambridge crystallographic structural database because of the highly ionic nature of these bonds (mean Na–F CCSD: 2.438; mean Na–N_{amido} CCSD: 2.442 Å)[43] and result in heavily distorted octahedral sodium geometries (N(4A)-Na(1A)-N(6A)# 148.0(1)°, N(3A)-Na(1A)-F(5A)# 94.4(1)°) and relatively symmetrical square-pyramidal fluoride environments (Na(1A)-F(1A)-Na(4A) 172.0(1), Na(1A)-F(1A)-Na(1A)# 88.1(1)°).

The increasing use of Group 1 amido complexes as synthetic reagents in inorganic chemistry and as strong Brønsted bases or nucleophiles in organic synthesis[86–89] has increased interest in the effect of Group 1 salts upon chemical reactivity. The high polarity of alkali metal M–X bonds (X = halide, amide etc) causes association of Group 1 species, yielding dimers, trimers or even oligomers that may become non-reactive or modify the activity of the host system.[44] The extent of this aggregation is largely dependent on the steric bulk of the associated ligands, although it has even greater dependence on metal charge density. For this reason, lithium salts, lithium bearing the highest charge density of all alkali metals, have received the most attention with regard to Group 1 inclusion compounds.[44, 90–99] Furthermore, in the absence of any tangible advantage to handling more reactive heavy Group 1 reagents, the wide-spread use of lithium reagents has led to almost all documented cases of Group 1 halide inclusion being those of lithium.[43] Non-serendipitous research into the entrapment of lithium salts has been principally advanced by the group of Chivers.[44, 95–99] Surplus to these forays, we are unaware of any concerning the chemistry of heavier Group 1 species. The selective preparation of **4** by reaction of HFPhF with excess sodium bis(trimethylsilyl)amide (see above) suggests that this study should be undertaken (see Scheme 2).

The molecular structure of compound **5**, like those of **1** and **3**, can be broken down into a dimeric unit of composition $M_2(FPhF)_2$ (Figure 5). Contrary to lighter metal analogues, and like potassium complexes of bulky *N*,*N*′-di(aryl)formamidinates, for example, [K{(η^6-Mes)NC(H)N(Mes)}{(η^6-Mes)NC(H)NH(Mes)}],[73] [K_2{(η^6-2,6-*i*Pr$_2$C$_6$H$_3$)NC(H)N-(2,6-*i*Pr$_2$C$_6$H$_3$)}$_2$(thf)$_2$] and [K{(η^6-2,6-*i*Pr$_2$C$_6$H$_3$)NC(H)N-(2,6-*i*Pr$_2$C$_6$H$_3$)}(thf)$_3$] · HFIso (HFIso; *N*,*N*′-di(2,6-diisopropylphenyl)formamidine),[78] the potassium centres of **5** exhibit a preference for potassium π-arene donation rather than supplementary nitrogen or solvent oxygen donors. This renders **5** Lewis-base-free and polymeric. As illustrated in Figures 5 and 6, compound **5** crystallises in the monoclinic space group $P2_1/n$ with half a dimeric $K_2(FPhF)_2$ in the asymmetric unit. Like **3**, within this dimeric unit, the NCN fragments coordinate the metal atoms in a $\mu_2{:}\eta^2{:}\eta^1$-binding

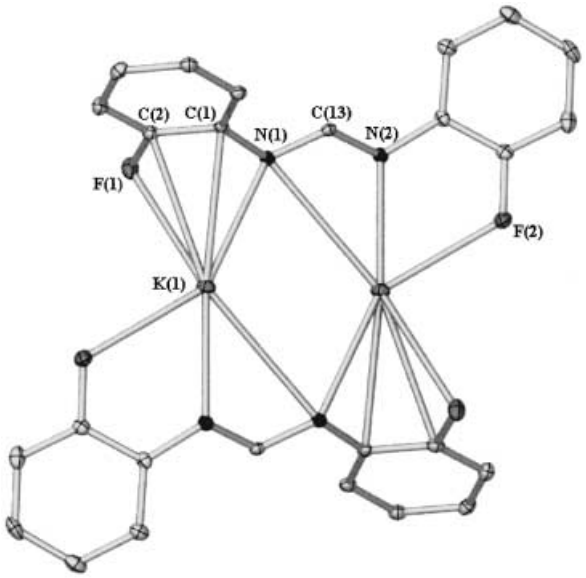


Figure 5. Molecular structure of a dimeric $K_2(FPhF_2)$ unit within [K{$\mu_4{:}\eta^4{:}\eta^3{:}\eta^2{:}\eta^1$-FPhF}$_\infty$] (**5**). Formamidinates exhibit ($\mu_2{:}\eta^4{:}\eta^3$-binding as shown. All hydrogen atoms omitted for clarity. Relevant bond lengths [Å] and angles [°]: K(1)–F(1) 3.030(4), K(1)–N(1) 2.934(5), K(1)–C(1) 3.199(5), K(1)–C(2) 3.255(6), K(1)#1–N(1) 3.444(5), K(1)#1–N(2) 2.767(5), K(1)#1–F(2) 2.805(4) N(1)–C(13) 1.322(7), N(2)–C(13) 1.323(7); F(1)-K(1)-N(1) 54.16(11), K(1)-N(1)-K(1)#1 66.34(9), N(1)-K(1)#1-N(2) 42.34(12), N(1)-K(1)#1-F(2) 99.33(11), N(2)-K(1)#1-F(2) 58.05(12), N(1)-C(13)-N(2) 123.5(5), F(1)-K(1)-F(2)#1 92.65(11), F(1)-K(1)-N(2)#1 147.89(12), F(1)-K(1)-N(1)#1 153.40(11), N(1)-K(1)-F(2)#1 146.12(12), N(1)-K(1)-N(2)#1 155.73(13), N(1)-K(1)-N(1)#1 113.66(9). Symmetry transformation used to generate #1 atoms: $-x+1, -y, -z$.

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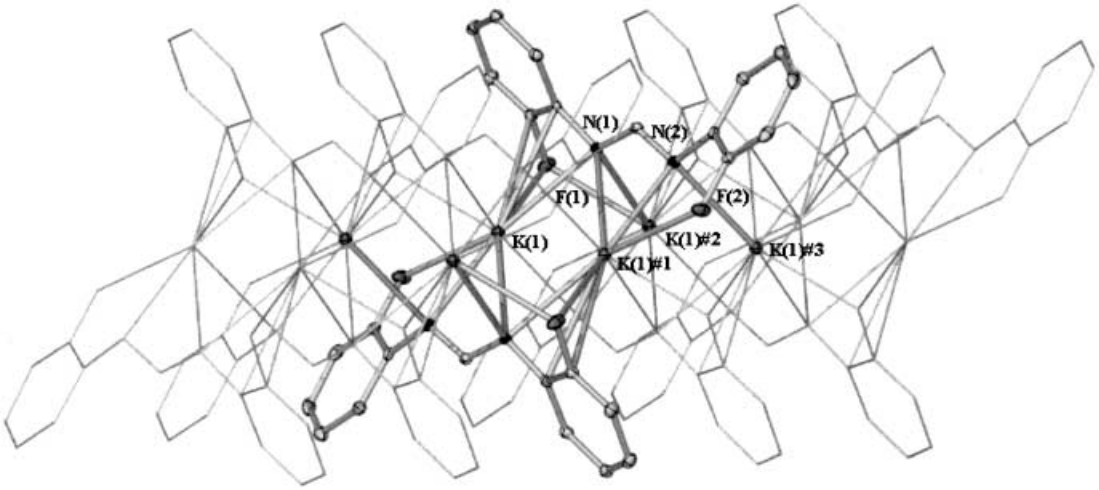

Figure 6. Macromolecular structure of $[K\{\mu_4:\eta^4:\eta^3:\eta^2:\eta^1\text{-FPhF}\}_\infty]$ (**5**). Dimeric unit of Figure 5 displayed as ellipsoids. Relevant bond lengths [Å] and angles [°] not listed in Figure 5: F(1)–K(1)#2 2.706(4), N(1)–K(1)#2 3.018(5), N(2)–K(1)#3 2.925(4), K(1)···K(1)#1 3.5155(21), K(1)···K(1)#2 3.9708(8), K(1)···K(1)#3 5.8124(22), K(1)#1···K(1)#2 4.7400(21), K(1)#1···K(1)#3 3.9708(8), K(1)#2···K(1)#3 3.5155(21); F(1)-K(1)#2-N(1) 56.34(11), K(1)-N(1)-K(1)#2 83.68(12), K(1)#1-N(1)-K(1)#2 94.12(12), K(1)#1-N(2)-K(1)# 88.44(13). Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y, -z$; #2: $x-1, y, z$; #3: $-x, -y, -z$.

mode giving K–N bond lengths of 2.767(5) (η^1) and 2.934(5), 3.444(5) Å (η^2) (see Figures 5 and 6). Like **4**, these interactions are supplemented by fluorine coordination of both *ortho*-fluoro groups. For F(1) this is K(1) (3.030(4) Å), and for F(2) this is K(1)# (2.805(4) Å). The aromatic group bearing the F(1) donor partakes in η^2-aryl donation to the K(1) metal centre (C(1)···K(1) 3.199(5) Å and C(2)···K(1) 3.255(6) Å). These lengths are extended with respect to those in the structural archive (mean K–C lengths of the potassium cyclopentadienide compound $[\{KCp(dme)_{0.5}\}_\infty]$: 3.055 Å;[100] mean K–C length in the CCSD: 3.116 Å);[43] but are well within the recognised limits set by compounds, like $[\{K(C(SiMe_3)_2C_6H_5)\}_\infty]$,[101] which possesses potassium arene–carbon bond lengths ranging from 3.093(2) to 3.522(2) Å. This provides the formamidinate ligand in **5** with greater asymmetry than those in **1** and **3**. In addition, the NCN backbone is opened to 123.5(5)° (**1** 122.0(2), **2** 121.8(2)°, HFPhF 122.5(1)°). Overall, this gives **5** the greatest dimer metal–metal distance amongst FPhF Group 1 metal complexes, namely 3.516(2) Å (cf. 3.234(8) in **1** and 3.285(2) Å in **2**), which suggests that the greater electropositivity and increased metallic radius of potassium (Allred and Rochow electronegativity of 0.9 (Li), 1.0 (Na), metallic radii 0.60 Å (Li), 1.00 Å (Na), 1.40 Å (K))[84] are predisposed to fluorine and arene-π donation. Similar potassium–arene interactions have been cited as stabilising influences in several organometallic systems that support unusual kinetically transient coordination environments.[102–105] Macromolecularly, the overlaying of $K_2(FPhF)_2$ dimeric units of **5** affords a polymeric structure that incorporates further formamidinate coordination to potassium atoms above and below the $K_2(FPhF)_2$ plane. As depicted in Figure 6, in tandem with augmentative bridging of F(1) to a proximal metal atom within the lattice (K(1)#2, F(1)-K(1)#2 2.706(4) Å), **5** is furnished with unprecedented tetranuclear bridging formamidinates that exhibit $\mu_4:\eta^4:\eta^3:\eta^2:\eta^1$-amidinate coordination. The bridging of four nuclei by one amidinate ligand is unique to **5** and the complex $[Li_4(\mu_4:\eta^1:\eta^1:\eta^1:\eta^1\text{-PhNC(Ph)NPh})(\mu_3:\eta^2:\eta^1:\eta^1\text{-PhNC(Ph)NPh})_2]$-$[Li(AlMe_3Bu^t)_2]$,[81] there being only three examples of trinuclear bridging amidinates in the Cambridge crystallographic structural database,[43, 80] whilst the macromolecular motif described by **5** exhibits metal–metal distances ranging from 3.516(2) to 5.812(2) Å. Furthermore, the recognised incorporation of lithium halides in lanthanoid species prepared by metathetical paths[106] make THf-soluble **5** an ideal precursor for the preparation of heteroleptic f-block *N*,*N*′-di(*ortho*-fluorophenyl)formamidinate species. These are currently under investigation.[82] Taking into account the macromolecular metal–ligand bond lengths (see Figure 6 caption), the bond lengths within the molecular structure of **5** possess mean values of 3.027 (K–N), 2.810 (K–F) and 3.227 Å (K–C). With the exception of the K–F bonds (which in the absence of donor solvent participate with potassium to a greater extent than the central metal atoms of **1** and **3**) these are elongated relative to those in the structural archive (2.939, 2.828 and 3.116 Å, respectively)[43] due to the decreased ligand–metal contact inherent of high nuclearity. Lastly, the fluorine coordination and η^2-aryl coordination of FPhF ligands in **5** provide an aryl–aryl torsion angle of 59.7(1)°; this is small compared with those of **1** and **3** (86.4(1)° and 85.7(1)°, respectively), which possess aryl groups that are not coordinated to fluorine. Interestingly, the layered solid-state motif of **5** (see Figure 6) would almost certainly be disrupted by the steric imposition of any group other than hydrogen upon the amidinate backbone.

Conclusion

We have demonstrated that the structural versatility of FPhF documented by complexes **1** and **3**–**5** epitomises the dextrous coordination of formamidinate ligands to contrasting metal assemblies. Comparisons with the chemistries of related *N*,*N*′-di(tolyl)formamidinate species[75, 77] indicate that the in-

creased NCN hapticity of FPhF results from fluoro substitution. This increases M···M distances and fully or partially frustrates the inclusion of ethereal donors that would intuitively decrease nuclearity. In tandem with the unencumbered nature of FPhF, not only caused by a hydrogen substituent upon the backbone but also the low steric demand of the *ortho*-fluorophenyl groups, this provides FPhF with a near autonomous binding preference without weakening the metal–nitrogen interaction (as evidenced by comparison with relevant Group 1 FTolP species, see above). In accordance, all species coordinate as per the coordinative requirements of the included metal centres, the perturbation of ideal 120° NCN-sp^2 centres largely depending on metal aggregation. In **4** and **5**, the sheer extent of this aggregation places increased demand upon the formamidinate frame. This results in disparate *ipso*-carbon-nitrogen-methyne carbon, NCN and *ipso*-carbon-nitrogen-metal angles that deviate in the ranges; 116.9(2)–119.6(2)°, 121.1(2)–121.4(2)°, 105.2(1)–135.9(1)° (**4**) and 115.1(4)–115.6(4)°, 123.5(5)°, 87.4(3)–120.8(3)° (**5**). The coordination preference of the FPhF ligands within **3** (μ_2:η^2:η^2) and **4** (μ_3:η^2:η^2:η^2) are unique with respect to the established precedent set by fluorinated formamidinate "lantern-type" complexes of chromium (μ_2:η^2:η^1).[79] Similarly, the binding motif of FPhF ligands within **5** (μ_4:η^4:η^3:η^2:η^1) is entirely unique in amidinate chemistry, a field of research that comprises elements spanning the periodic table.

Experimental Section

The formamidinate ligand precursor *N,N'*-di(*ortho*-fluorophenyl)formamidine, HFPhF, was synthesised according to a published procedure.[8, 107] *n*-Butyllithium (1.6 M solution in hexanes), sodium bis(trimethylsilyl)amide (1.0 M solution in tetrahydrofuran) and potassium bis(trimethylsilyl)amide (0.5 M solution in toluene) were purchased from Aldrich. Tetrahydrofuran, diethyl ether and hexane were dried over sodium, freshly distilled from sodium/benzophenone ketyl and freeze–thaw degassed prior to use. Toluene was dried over sodium, freshly distilled from Na/K alloy and freeze–thaw degassed prior to use. All manipulations were performed by means of conventional Schlenk or glove-box techniques under an atmosphere of high purity dinitrogen in flame-dried glassware. Infrared spectra were recorded as Nujol mulls between sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra were recorded at 75.5 MHz and ^{19}F{^{1}H} NMR spectra at 282 MHz on a Bruker BZH300/52 spectrometer, with chemical shifts referenced to the residual ^{1}H, ^{13}C resonance signals of the deuterated benzene solvent or, for ^{19}F{^{1}H} NMR spectra, an external CCl_3F standard ($\delta = 0.0$). Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Microanalyses for compounds **1**, **2** and **5** were conducted at the University of Otago (New Zealand) The high solvent dependency of compounds **3** and **4** (loss of crystallinity within seconds upon removal from mother liquor), combined with their pronounced sensitivity to moisture and air, prevented the acquisition of meaningful C,H,N microanalytical data. However, given that ^{1}H NMR spectra of **3** and **4** show no observable impurities, and in view of the sharpness of their melting points, we believe the bulk purity of both to be of microanalytical quality. A resonance attributable to the bound NaF moieties of compound **4** was not observed, and is thought to be placed beyond the range of the spectrometer employed (see above).

[{Li(μ_2:η^2:η^1-FPhF)(thf)}$_2$] (1): *n*-Butyllithium (0.80 mL, 1.28 mmol) was added dropwise to a solution of HFPhF (0.30 g, 1.29 mmol) in THF (40 mL). This resulted in the formation of a light yellow solution that was stirred overnight at ambient temperature. The solution was concentrated in vacuo (≈10 mL), filtered and stored at −10 °C overnight to yield the title compound as small colourless blocks. Yield: 0.27 g (68 %); m.p. 121 °C; ^{1}H NMR (C_6D_6, 300 K): $\delta = 1.44$ (m, 8H; CH_2, THF), 3.62 (m, 8H; CH_2O, THF), 6.66 (m, 4H; Ar-H), 6.84 (m, 8H; Ar-H), 7.08 (m, 4H; Ar-H), 8.07 ppm (br s, 2H; NC(H)N); ^{13}C NMR (C_6D_6, 300 K): $\delta = 26.1$ (s; CH_2, THF), 68.3 (s; CH_2O, THF), 115.6, 115.8, 121.5, 122.8 (br s; Ar-C), 125.3 (d, J(C,F) = 3.4 Hz; Ar-C), 137.5 (s; Ar-C), 158.4 ppm (s; NC(H)N); ^{19}F{^{1}H} NMR (C_6D_6, 300 K): $\delta = -126.7$ ppm (s); IR (Nujol): $\tilde{\nu} = 670$ (w), 756 (m), 804 (m), 843 (m), 884 (m), 920 (m), 991 (m), 1035 (m), 1101 (m), 1188 (m), 1216 (s), 1277 (m), 1338 (m), 1486 (s), 1561 (s), 1618 (m), 1672 (m) cm^{-1}; elemental analysis (%) calcd for $C_{34}H_{34}N_4O_2F_4Li_2$: C 65.81, H 5.52, N 9.03; found: C 65.86, H 5.48, N 9.47.

[Na(FPhF)(thf)] (2): Sodium bis(trimethylsilyl)amide (2.50 mL, 2.50 mmol) was added dropwise to a solution of HFPhF (0.57 g, 2.45 mmol) in THF (20 mL). The resulting solution was stirred overnight. Volatiles were removed in vacuo to render an oil that precipitated as a light powder upon washing with toluene (≈2 mL). The powder was extracted into fresh THF (15 mL), and the mixture was filtered and stored at −5 °C to yield the title compound as a colourless microcrystalline powder. Yield: 0.55 g (69 %); m.p. 265 °C, decomposition 290 °C; ^{1}H NMR (C_6D_6, 300 K): $\delta =$ 1.43 (m, 4H; CH_2, THF), 3.59 (q, 4H; OCH_2, THF), 6.61 (m, 2H; Ar-H), 6.85 (m, 6H; Ar-H), 8.65 ppm (br s, 1H; NC(H)N); ^{13}C NMR (C_6D_6, 300 K): $\delta = 24.4$ (*s*; CH_2, THF), 66.6 (s; OCH_2, THF), 113.6, 113.9, 118.9, 119.0, 123.9, 142.7 (br s; Ar-C), 162.6 ppm (s; NC(H)N); ^{19}F{^{1}H} NMR (C_6D_6, 300 K): $\delta = -135.9$ ppm; IR (Nujol): $\tilde{\nu} = 610$ (w), 741 (m), 804 (m), 841 (m), 884 (w), 924 (m), 1002 (m), 1039 (m), 1099 (m), 1149 (w), 1220 (s), 1261 (m), 1274 (m), 1486 (s), 1546 (s), 1617 (m) cm^{-1}; elemental analysis (%) calcd for $C_{17}H_{17}N_2O_1F_2Na_1$: C 62.57, H 5.25, N 8.58; found: C 62.02, H 5.24, N 9.01.

[{Na(μ_2:η^2-FPhF)(Et$_2$O)}$_2$] (3): Sodium bis(trimethylsilyl)amide (2.50 mL, 2.50 mmol) was added dropwise to a solution of HFPhF (0.57 g, 2.45 mmol) in Et_2O (25 mL) at −50 °C. The resulting solution was stirred for 3 h at low temperature before warming to ambient temperature. The mixture was stirred overnight, and volatiles were removed in vacuo to yield a light coloured powder. The powder was extracted into fresh diethyl ether (15 mL), and the mixture was filtered and stored at −5 °C to yield the title compound as small colourless prisms. Yield: 0.57 g (71 %); m.p. 238 °C, decomposition 290 °C; ^{1}H NMR (C_6D_6, 300 K): $\delta = 1.18$ (t, 12H; CH_3, Et_2O), 3.27 (q, 8H; OCH_2, Et_2O), 6.63 (m, 4H; Ar-H), 6.86 (m, 12H; Ar-H), 8.58 ppm (br s, 2H; NC(H)N); ^{13}C NMR (C_6D_6, 300 K): $\delta = 14.2$ (s; CCH_3, Et_2O), 64.6 (s; OCH_2, Et_2O), 113.7, 114.1, 119.3, 120.1, 124.1, 141.1 (br s; Ar-C), 156.6 ppm (s; N*C*(H)N); ^{19}F{^{1}H} NMR (C_6D_6, 300 K): $\delta = -136.3$ ppm; IR (Nujol): $\tilde{\nu} = 610$ (w), 741 (m), 805 (m), 841 (m), 885 (w), 923 (m), 1034 (m), 1098 (m), 1150 (w), 1223 (s), 1275 (m), 1299 (m), 1487 (s), 1566 (s), 1617 (m) cm^{-1}.

[{Na$_3$(μ_3:η^2:η^2:FPhF)$_3$(NaF)(μ_2-Et$_2$O)}$_2$] (4): Sodium bis(trimethylsilyl)amide (1.70 mL, 1.70 mmol) was added dropwise to a solution of HFPhF (0.40 g, 1.72 mmol) in Et_2O (40 mL) at ambient temperature. The resulting light yellow solution was stirred overnight, then all volatiles were removed in vacuo to render a colourless powder that was washed with cold hexane (3 × 15 mL). The dried material was extracted into fresh diethyl ether (10 mL), filtered and stored at −5 °C to fractionally crystallise **4** as colourless needles. Yield: 0.19 g (51 % by Na); m.p. 226 °C (decomp); ^{1}H NMR (C_6D_6, 300 K): $\delta = 1.36$ (t, 12H; CH_3, Et_2O), 3.56 (q, 8H; OCH_2, Et_2O), 6.67 (m, 12H; Ar-H), 6.82 (m, 24H; Ar-H), 7.08 (br m, 12H; Ar-H), 8.49 ppm (br s, 6H; NC(H)N); ^{13}C NMR (C_6D_6, 300 K): $\delta = 14.4$ (s; CCH_3, Et_2O), 66.6 (s; OCH_2, Et_2O), 114.6, 114.9, 120.6, 122.7, 128.3, 138.5 (br s; Ar-C), 152.9 ppm (s; NC(H)N); ^{19}F{^{1}H} NMR (C_6D_6, 300 K): $\delta =$ −137.2 ppm; IR (Nujol): $\tilde{\nu} = 608$ (w), 745 (m), 810 (m), 836 (m), 1040 (m), 1097 (m), 1231 (m), 1286 (m), 1310 (m), 1446 (s), 1567 (s), 1610 (m), 1687 (w) cm^{-1}.

[{K(μ_4:η^4:η^3:η^2:η^1-FPhF)}$_8$] (5): Potassium bis(trimethylsilyl)amide (2.6 mL, 1.30 mmol) was added dropwise to a stirred solution of HFPhF (0.30 g, 1.29 mmol) in THF (30 mL) resulting in immediate precipitation of a light coloured material. After stirring for 3 h, all volatiles were removed in vacuo to yield a colourless opaque oil. Washing with hexane (3 × 5 mL) gave a clean precipitate that was extracted into fresh THF (20 mL). The mixture was concentrated in vacuo and filtered. The filtrate was stored at −25 °C overnight to yield the title compound as colourless blocks. Yield: 0.30 g (86 %); m.p. 234 °C; ^{1}H NMR (C_6D_6, 300 K): $\delta = 6.77$ (m, 2H; Ar-H), 7.05 (m, 6H; Ar-H), 8.58 ppm (br s, 1H; NC(H)N); ^{13}C NMR (C_6D_6, 300 K): $\delta = 114.2$ (d, J(C,F) = 21.5 Hz; Ar-C), 119.0, 119.3 (br s; Ar-C),

0947-6539/03/0902-0422 $ 20.00+.50/0 *Chem. Eur. J.* **2003**, *9*, No. 2

124.1 (d, J(C,F) = 3.2 Hz; Ar-C), 128.0 (br s; Ar-C), 142.0 (d, J(C,F) = 9.2 Hz; Ar-C), 161.4 ppm (s; NC(H)N); ^{19}F{^{1}H} NMR (C_6D_6, 300 K): δ = −130.5 ppm; IR (Nujol): $\tilde{\nu}$ = 606 (m), 650 (w), 753 (m), 804 (m), 838 (m), 890 (w), 922 (m), 991 (m), 1035 (m), 1098 (m), 1153 (w), 1180 (m), 1217 (s), 1328 (s), 1464 (s), 1538 (s), 1614 (m) cm^{-1}; elemental analysis (%) calcd for $C_{13}H_9N_2F_2K_1$: C 57.76, H 3.36, N 10.36; found: C 57.70, H 3.65, N 10.11.

X-ray crystallography: Crystalline samples of compounds **1** and **3**–**5** were mounted upon glass fibres, in viscous hydrocarbon oil, at −150 °C (123 K). Crystal data were obtained on an Enraf-Nonius Kappa CCD. Data were corrected for absorption with the DENZO program.[108] Structural solution and refinement was carried out with the SHELX suite of programs[109] and the graphical interface X-Seed.[110] All hydrogen atoms were placed in calculated positions by the riding model. Crystal data and refinement parameters for all complexes are compiled in Table 1.

CCDC-191157 (**1**), CCDC-191158 (**3**), CCDC-191159 (**4**) and CCDC-191160 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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