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Potassium complexes of the 'super' formamidine (2,6-$Pr^i_2C_6H_3$)NC(H)NH(2,6-$Pr^i_2C_6H_3$), HDippForm. Synthesis and molecular structure of [{K(DippForm)$_2$K(THF)$_2$}$_n$]·nTHF and [K(DippForm)(THF)$_3$]·HDippForm

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Dedicated to Professor Jerry L. Atwood on the occasion of his 60th birthday in recognition of his outstanding contribution to the fields of supramolecular and organometallic chemistry

Abstract

Ambient temperature treatment of the formamidine (2,6-$Pr^i_2C_6H_3$)NC(H)NH(2,6-$Pr^i_2C_6H_3$), HDippForm, with one equivalent of potassium bis(trimethylsilyl)amide yields the formamidinate species [{K(DippForm)$_2$K(THF)$_2$}$_n$]·nTHF (**1**), which exhibits a macromolecular structure of alternating η^6-arene:η^1-amide bound potassium di-amidinate and potassium di-THF units in a one-dimensional polymeric array. Addition of a further equivalent of HDippForm to **1** affords hydrogen bound [K(DippForm)(THF)$_3$]·HDippForm (**2**). The supramolecular structure of **2** resembles a 'topochemical' arrangement of K(DippForm) and HDippForm moieties that, in tandem with ^{1}H-NMR data, corroborate a putative [K(DippForm)(HDippForm)] composition in solution.

Keywords: Potassium; Amidinates; Coordination modes; Nitrogen donors

1. Introduction

In recent years there has been a renaissance in amidinate chemistry of the main group elements [1–15]. Taking into account ground breaking olefin polymerisation studies [16–18] pioneered by Jordan et al. [19–21], which utilise robust aluminium alkyl amidinate species, one can safely say that main group metal amidinates are no longer hampered with the label of metathesis reagents for the preparation of their more illustrious transition metal cousins. However, in spite of these developments, it remains that the coordinative diversity observed for amidinates bound to main group elements is overwhelmingly out-weighed by that of d-block systems [22]. Indeed, aside from alkali metal and cationic Group 13 amidinate species; e.g. [{Na(μ_2:η^2:η^1-DTolFormP)(DME)}$_2$] [23] (DTolFormP = *N*,*N*′-di(*para*-tolyl)formamidinate) and [Al_2Me_3{μ_2:η^2:η^1-$Pr^iNC(CH_3)NPr^i$}$_2$][$B(C_6F_5)_4$] [20], all reported amidinate complexes of the main group elements exhibit either η^2-chelated or μ_2:η^1:η^1-bridged amidinate binding modes [24]. This almost certainly reflects the decrease in polarity and increase in covalent character for M–N bonds of the p-block elements, greater structural diversity being characteristic of ionic systems.

To address this, reports from the groups of Arnold [25–28] and Lappert [29–31], and crystallographic studies undertaken in our laboratory have extended the binding remit of amidinate ligands for 'non-transition metal' based systems [32–36]. This includes amidinate coordination modes that were hitherto unknown for d-block elements, e.g. that of the first structurally authenticated formamidinate complex of lithium; [{Li(μ_2:η^2:η^1-DTolFormP)(Et_2O)}$_2$] [37], and the novel di-potassium di-μ_2:η^2:η^2-amidinate motif of species like [{K((C_6H_{11})NC{N($SiMe_3$)$_2$}N(C_6H_{11}))}$_2$] [26] and

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[{K_2(DTolFormP)$_2$(μ_2-THF)$_3$}$_n$] [34]. Furthermore, earlier this year we reported a new binding mode for *N*,*N*′-di(aryl)amidinates that capitalises upon the affinity of potassium for π-arene interactions; [K(η^6:η^1-DMesForm)(η^6:η^1-HDMesForm)] (**3**) (HDMesForm/DMesForm = *N*,*N*-di(2,4,6-trimethylphenyl)formamidine/ate) [32]. In compound **3**, the metal atom is bound by imine/amide and η^6-arene interactions from each ligand. This unusual motif results from the steric imposition of mesityl(2,4,6-trimethylphenyl) groups, which frustrate the archetypal μ_2:η^2:η^2-binding exhibited by all other amidinate complexes of potassium [29,30,32,34]. This encumbrance also affects suppression of reactivity for the included HDMesForm moiety, which does not react even in the presence of excess transamination reagent or a recognised strong Lewis base donor. As such, compound **3** represents the first example of a Group 1 metal amine complex that possesses suppressed deprotonation borne out of steric and π-arene stabilisation [38].

The use of sterically encumbered substituents to isolate kinetically transient low-valent species of the main group elements [39–42], most notably those of gallium [43–46], is an area of significant academic interest. In these cases, it is recognised that the imposed steric bulk of such ligands often incites modification of orthodox bonding and metal assembly. Attempts to apply the same rationale to species of known kinetic and thermodynamic stability in order to modify reactivity and structure, as in the use of DMesForm in **3** versus the use of the sterically 'slight' DTolFormP in [{K_2(DTolFormP)$_2$(μ_2:η^2:η^1-DME)$_2$}$_n$] [32,34], have been sparse (DME = 1,2-dimethoxyethane) [47]. To advance our study of increased steric bulk and its effect upon formamidinate binding in alkali metal systems, we now report the reaction of the new 'super' formamidine (2,6-$Pr^i_2C_6H_3$)NC(H)NH(2,6-$Pr^i_2C_6H_3$), HDippForm, with potassium bis(trimethylsilyl)amide. The implications of 2,6-isopropyl substituents with regard to **3** are discussed. These studies suggest the chemical inertness and metrical parameters of **3** are disturbed rather than reinforced by increased bulk at the arene 2,6-positions. With the exception of [{K{μ_2:η^5:η^4-(2,6-$Pr^i_2C_6H_3$)NC(Me)C(H)C(Me)N(2,6-$Pr^i_2C_6H_3$)}}$_n$·$n$$C_6H_5CH_3$] [48], reports of Group 1 homometallic complexes that contain a bound uninegative nitrogen ligand bearing the 2,6-$Pr^iC_6H_3$ group (Dipp) have been hitherto restricted to lithium [49–54].

2. Results and discussion

Unlike the analogous HDMesForm reaction [32], potassium bis(trimethylsilyl)amide reacts with one equivalent of HDippForm in THF to yield a crystalline compound (**1**) that is devoid of the ^{1}H- and ^{13}C-NMR resonances (d_8-THF) and FTIR stretches associated with protonation. For [(HDippForm)$_2$], these appear at 9.45 ppm (^{1}H-NMR d_8-THF, N*H*), 147.7 ppm (^{13}C-NMR d_8-THF, N*C*(H)N) and 3002 cm^{-1} (FTIR, N–H stretch). The methyne proton resonance (NC(H)N) experiences a downfield shift to 8.87 ppm ([(HDippForm)$_2$] 7.28 ppm), which is indicative of deprotonation whereby the anionic charge of the NCN backbone shields this proton [34]. Comparisons to the ^{1}H-NMR methyne proton resonances of **3** [32] and the related species [{K_2(μ_2:η^2:η^2-DTolFormP)$_2$(μ_2-THF)$_3$}$_n$] (**4**) [34] (9.13, 8.13 ppm respectively) suggest the formamidinate ligands of **1** participate in η^6:η^1-binding, as-per the DMesForm ligands of **3**, however, unlike **3** the absence of protonated ligands in **1** demands that suppression of HDippForm reactivity does not occur. This is also alluded to by the inclusion of THF in **1** (1:1 with DippForm ligands), the inclusion of HDMesForm rendering **3** solvent donor free [32].

To elucidate the DippForm binding exhibited by **1**, crystalline samples of suitable quality for X-ray structure determination were grown from THF. The molecular structure of **1**, [{K(DippForm)$_2$K(THF)$_2$}$_n$]·nTHF, can be seen in Fig. 1 (POV-Ray illustration, 30% thermal ellipsoids), whilst relevant bond lengths and angles are listed in Table 1. Compound **1** crystallises in the monoclinic space group $P2_1/m$ with half a potassium di-formamidinate potassium di-THF moiety and half a THF of solvation in the asymmetric unit. Macromolecularly, these units tether one another to form an indefinite *pseudo* anion–cation polymer. Superficially, this bares a structural resemblance to the cation anion pairs of [Li(DME)$_3$][Li$_2$(μ_2:η^1:η^1-DTolFormP)$_3$] [23] and [Li(DME)$_3$][Li(η^2-DTolFormO)$_2$] [35] (DTolFormO = *N*,*N*′-di(*ortho*-tolyl)formamidinate), however, the binding of the K(DippForm)$_2$ units in **1** is of most interest. Like **3** [32] and the *N*,*N*′-di(*ortho*-fluorophenyl)formamidinate species [{K(μ_4:η^4:η^3:η^2:η^1-(2-FC_6H_4)NC(H)N(2-FC_6H_4))}$_8$] [36], this moiety demonstrates a preference for π-arene interactions over conventional ethereal donation. This manifests itself as two η^6:η^1-bound DippForm ligands, congruent to the DMesForm in **3** [32], which interact such that the η^6-interactions diametrically oppose one another (centroid–K(1)–centroid angle 180.0°, prerequisite of crystallographic symmetry). When combined with the amide interactions, this produces a square planar potassium environment (N(2)–K(1)–N(2)# 180.0, N(2)–K(1)–centroid 79.8(2), N(2)#–K(1)–centroid 100.2(2)°, total of angles about K(1) 360.0°), of which the metal resides in the N_2centroid$_2$ plane. Although the DMesForm and HDMesForm ligands of **3** describe similar binding to **1**, the relative orientation of the less encumbered ligands radically differs (see Table 1) [32]. In **3**, the NCN and N–K–centroid planes of the HDMesForm and DMesForm ligands exist at relative angles of 72.9(9) and

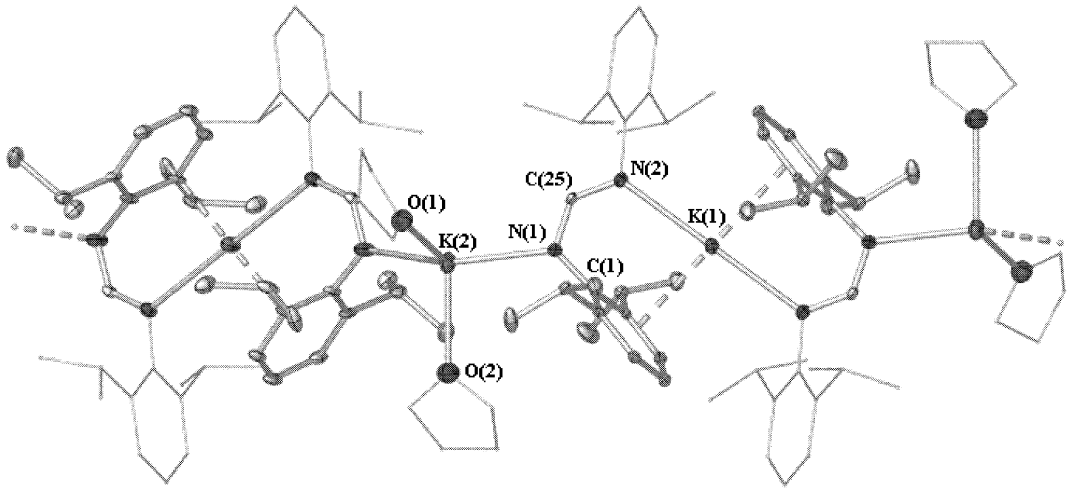

Fig. 1. Molecular structure of $[\{K(DippForm)_2K(THF)_2\}_n]\cdot n$THF (**1**). THF of solvation and all hydrogen atoms are omitted for clarity. Relevant bond lengths and angles are listed in Table 1.

78.3(2)° (**1**; 0 and 0°, respectively, as required by crystallographic symmetry), whilst the centroid–K–centroid angle is lessened to 122.6(2)° [32]. This furnishes the central metal of **3** with a heavily distended tetrahedral geometry and superior formamidinate ligand–metal proximity, as can be seen by the metal-to-centroid distances of 3.034(9) (**1**) and 2.887(8) Å (**3**) [32] (mean K–C contact of **1**; 3.31 Å, comparable to mean carbon–potassium contact of $[\{K\{\mu_2:\eta^5:\eta^4\text{-}(2,6\text{-}Pr^i_2C_6H_3)NC(Me)C(H)C(Me)N(2,6\text{-}Pr^i_2C_6H_3)\}\}_n\cdot nC_6H_5CH_3]$; 3.33 Å [48], greater than mean K–C bond length of $[K_4(\mu_2:\eta^2:\eta^1\text{-}DME)_2(\mu_4:\eta^5:\eta^5:\eta^1:\eta^1\text{-}C_5H_5)(\mu_2:\eta^5:\eta^5\text{-}C_5H_5)_3]$; 3.055 Å [54], but less than K–C lengths of up to 3.522(2) Å in $[\{K(C(SiMe_3)_2\text{-}C_6H_5)\}_8]$) [55], and differing metal–amide lengths of 2.863(4) (**1**) and 2.719(2) Å (**3**) ((**1**); K(1)–N(1) 4.019(4) Å, K–N lengths of $[\{K\{\mu_2:\eta^5:\eta^4\text{-}(2,6\text{-}Pr^i_2C_6H_3)NC(Me)\text{-}C(H)C(Me)N(2,6\text{-}Pr^i_2C_6H_3)\}\}_n\cdot nC_6H_5CH_3]$; 2.639(2) and 2.740(2) Å) [48]. In spite of this, the degree of electron delocalisation across the NCN backbone of **1** is not perturbed by reduced interaction (N(1)–C(25) 1.315(6), N(2)–C(25) 1.321(6) Å, for **3**; 1.319(2) and 1.324(2) Å [32], for $[(HDippForm)_2]$; C=N 1.260(5), C–N 1.352(5) Å) [56]. Intuitively, the orientation of the formamidinate units in **1** generates the least steric buttressing (see Fig. 1), however, the preference for arene and not ethereal donors, and therefore the existence of two metal environments, is highly unorthodox. The '*quasi*-cation' metal centre of **1**, K(2), resides in a distorted tetrahedral pocket (O(1)–K(2)–O(2) 113.1(2), N(1)–K(2)–N(1)# 149.5(2), N(1)–K(2)–O(2) 96.6(1)°) composed of two terminal THF donors (K(2)–O(1) 2.668(5), K(2)–O(2) 2.677(6) Å, mean K–O of bridging THF ligands in **4**; 2.82 Å) [34] and two *pseudo*-imine donors from the $K(DippForm)_2$ units (K(2)–N(1)/N(1)# 2.687(4), K(2)–N(2)/N(2)# 4.767(4) Å). The K–N bond length from the latter is characteristically short relative to that of the '*quasi*-anion' metal centre due to decreased steric congestion and coordination number and increased overall cationic charge ('*quasi*-anion' composed of one potassium and two $\eta^6{:}\eta^1$-chelated DippForm units), however, although it is convenient to view the polymer of **1** as tethered $KDippForm_2$ anions and $K(THF)_2$ cations, the abated length of K(2)–N(1) relative to K(1)–N(2) does some-

Table 1
Selected bond lengths (Å), angles (°) and torsion/dihedral angles (°) for the K(formamidinate) units of complexes **1**–**4**, for complex **3** only DMesForm ligand listed

	1	**2**	**3** [32]	**4** [34]
K–N	2.863(4)	2.756(2)	2.719(2)	2.919 [c,d]
K–arene centroid	3.034(9)	2.987(12)	2.887(8)	–
NCN C–N(1)	1.315(6)	1.312(3)	1.319(2)	1.328(3) [c]
NCN C–N(2)	1.321(6)	1.319(3)	1.324(2)	1.328(3) [c]
K–K# [a]	6.693(1)	15.753(4)	10.191(2)	3.689 [d]
Mean K–O	2.673	2.692	2.692	2.82
N–K–centroid	79.8(2)	79.0(3)	84.8(3)	–
N#–K–centroid [b]	100.2(2)	–	126.8(2)	–
Centroid–K–centroid	180.0	–	122.6(2)	–
NCN N(1)–C–N(2)	128.3(4)	126.5(2)	126.3(2)	121.8(2) [c]
η^6-Arene plane: NCN	89.6(4)	83.4(3)	88.5(2)	–
Non-η^6-arene plane: NCN	79.8(4)	72.4(4)	65.9(2)	26.01 [d]
NN vector: η^6-arene plane	91.0(3)	89.3(3)	91.9(8)	–
NN vector: non-η^6-arene plane	140.3(3)	145.2(3)	144.3(9)	146.7
NCN plane: NCN plane	0.0	8.6(9) [e]	72.9(9)	11.9
N–K–N# [b]	180.0	–	112.3(1)	46.96 [c,d]
η^6-arene plane: η^6-arene# plane [b]	0.0	–	48.2(1)	25.68(8) [c,f]

Symmetry transformations used to generate equivalent atoms: [a]For **2**; $1/2+x$, $1/2-y$, $z-1/2$. For **3**; x, $y-1$, z. [b]For **1**; $-x$, $-y$, $1-z$. [c]For one DTolFormP ligand within the $[\{K_2(\mu_2:\eta^2:\eta^2\text{-}DTolFormP)_2(\mu\text{-}THF)_3\}_8]$ polymer. [d]Mean value. [e]To non-coordinated HDippForm NCN backbone plane. [f]Non-η^6-arene plane: non-η^6-arene plane angle.

what refute the apportioning of K–N_{imino} and K–N_{amido} status to each interaction. As they are both significantly shorter than the mean K–N bond deposited in the CCDC (mean bond length K–N 2.939 Å) [24], both are deserving of potassium–amido classification. In tandem with the K(DippForm)$_2$ units, the *quasi*-ionic composition of **1** creates a significantly greater K···K distance (6.693(1) Å) than that of the di-potassium di-amidinate units of **4** (mean K···K 3.689 Å, intra-K_2DTolFormP$_2$ K···K 3.455(1) Å) [34]. This can also be attributed to the greater steric congestion of **1**, which frustrates closer contact of the units and leads to opening of the NCN backbone angle to 128.3(4)° (DMesForm of **3**; 126.3(2)°) [32], almost orthogonal placement of the 2,6-$Pr^i_2C_6H_3$ planes to the NCN backbone (η^6; 89.6(4), non-η^6; 79.8(4), **3**; 88.5(2) and 65.9(2)°, respectively) [32] and disparate angles of the chelated and non-chelated aryl rings to the N–N vector of the formamidinate NCN backbone (η^6; 91.0(3), non-η^6; 140.3(3), **3**; 91.9(8), 144.3(9)°, respectively) [32]. In view of the greater steric protection afforded by DippForm the absence of suppressed reactivity for HDippForm when reacted with [K{N(SiMe$_3$)$_2$}], unlike that seen for HDMesForm in **3** [32], must result from preclusion of the necessary metal–ligand contact, i.e. the steric bulk of DippForm is too great. Furthermore, the existence of a singular broadened arene environment in ^{1}H-NMR spectra of **1** (broad singlet, 7.06 ppm) ascribes to either fluxional redistribution of the bound ligands or a differing solution state structure, e.g. η^2-chelation (the latter is not consistent with NCN methyne ^{1}H-NMR data, see above). Low temperature ^{1}H-NMR (d_8-THF $T = 223$ K) identifies the origin of the equivalence as redistribution, wherein, akin to **3**, differing aryl environments, one at higher field (non-coordinated) and one at lower field (coordinated), become evident (see below). This is in accordance with **3** [32] and consistent with the retention of solid-state structure in solution.

In order to fully compare the solution state nature of a DippForm species with **3**, and perhaps elucidate why deprotonation of HDippForm is not suppressed, the attempted generation of a [K(DippForm)(HDippForm)] species was undertaken. To maximise observation of this, two equivalents of HDippForm were added to a d_8-THF solution of **1**. Like those of **1** and **3**, the ^{1}H-NMR spectrum of this solution (298 K) displays a single broadened arene environment without sharp [(HDippForm)$_2$] resonances (e.g. N*H* resonance at 9.45 ppm). This is consistent with the inclusion of HDippForm and redistribution about the potassium core. Such redistribution is diminished at low temperature ($T = 233$ K) whereupon aromatic resonances at 6.86, 7.06 and 7.15 ppm (broad multiplets, previously one multiplet at 7.08 ppm, see Section 3), integrating to 4, 2 and 6 protons, respectively, are observed (broad N*H* resonance of HDippForm at 9.27 ppm). These are reminiscent of the non-coalesced aromatic resonances of **1** (6.59, 6.70 and 7.05 ppm, 4H, 6H and 2H, respectively) and thus ascribe to the formation of a '**3**-like' [K(DippForm)(HDippForm)] unit for **2** in solution.

To assess the identity of **2**, and whether it indeed resembles **3** [32], a bulk sample of compound **1** was treated with HDippForm (2.0 molar equivalents) and the resultant material fully investigated. This gave a colourless micro-crystalline solid that characterised as [K(DippForm)(HDippForm)(THF)$_3$] by ^{1}H-NMR (spectra congruent to those above) and displayed an amino stretch at 3106 cm^{-1}, which is considerably shifted with respect to that of the free HDippForm ligand (3002 cm^{-1}) [56]. Furthermore, the thermal stability of compound **2** exceeds that of **1** (m.p. (dec.) 288, 247 °C, respectively), which is in turn greater than the melting point of [(HDippForm)$_2$] (201 °C) [56]. Crystalline samples of **2** of suitable quality for XRD were grown from THF and a structure determination undertaken (see Fig. 2, POV-RAY illustration, 30% thermal ellipsoids).

Compound **2** crystallises in the monoclinic space group $P2_1/n$ with a single η^6:η^1-DippForm ligand and three THF ligands bound to a potassium centre and a protonated HDippForm formamidine in the asymmetric unit. Table 1 includes relevant metrical parameters for the η^6:η^1-bound DippForm unit of **2** (as well as relevant measurements for **3** and **4**) [32,34], these are similar to **1** and will not be discussed further. However, of note, the potassium atom of **2** resides in a trigonal bipyramidal environment (**1** square planar, **3** tetrahedral) that exhibits angles of; centroid–K(1)–O(1) 176.7(1), N(1)–K(1)–O(1) 97.9(1), N(1)–K(1)–O(3) 125.3(1)°, and K–O bond lengths of; 2.693(2), 2.700(2) and 2.682(2) Å (O(1), O(2) and O(3), respectively).

Unlike **3**, the protonated formamidine ligand is not included in the metal coordination-sphere of **2**, instead it is hydrogen bound to the *pseudo*-imine nitrogen of the coordinated DippForm ligand (via amino proton; N(1A)–H(1A)···N(2) 171.1°, N(1A)–H(1A) 0.902, H(1A)···N(2) 1.89(6), N(1A)···N(2) 2.782(6) Å). As suggested for **1**, this probably results because the steric requirements of the HDippForm/DippForm ligand prohibit the metal–ligand proximity necessary for a stable [K(DippForm)(HDippForm)] unit that would otherwise possibly suppress HDippForm reactivity. Irrespective, given the inferred coordination of HDippForm whilst in solution (^{1}H-NMR) and the solid-state structure of **1**, which contains K(DippForm)$_2$ units, the solid-state identity of **2** is counterintuitive. The explanation for this must lie in the absence of metal–amide formation of a [K(DippForm)$_3$] anion, whereby appending the ligand would reduce/nullify lability. Accordingly, one can surmise that HDippForm coordination is inherently flawed in the solid-state when pitched against the less invasive coordination of tetrahydrofuran. In-

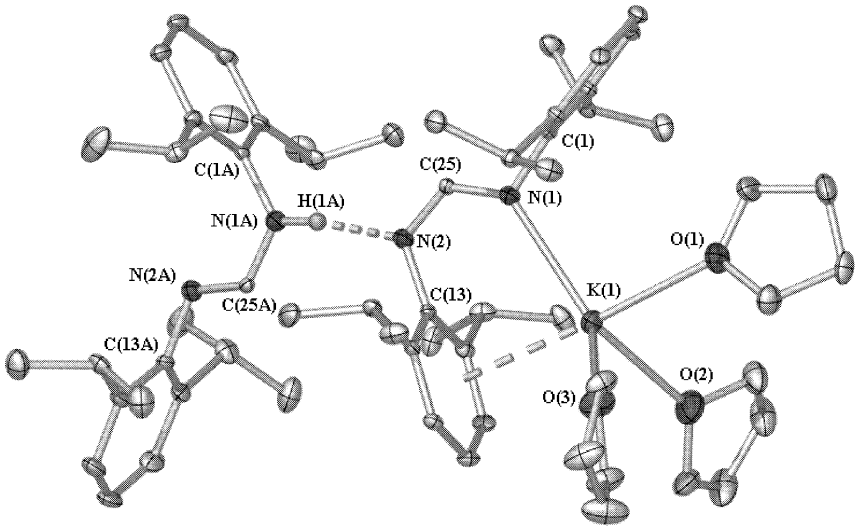

Fig. 2. Molecular structure of [K(DippForm)(THF)$_3$]·HDippForm (**2**). All hydrogen atoms except H(1A) are omitted for clarity. Relevant bond lengths and angles are listed in Table 1.

deed, this is alluded to by the supramolecular placement of [K(DippForm)(THF)$_3$]·HDippForm units within the crystal lattice of **2**, see Fig. 3 (POV-RAY illustration, 30% thermal ellipsoids). As depicted, the approach of these is reminiscent of the K(DippForm)$_2$ units of **1**, whereby the HDippForm ligands appear 'topochemically' organised at angles that approximate the placement of 'secondary' DippForm ligands in **1** (NCN:NCN plane torsion angle; 8.3(9), **1**; 0°). One could argue that this is simply an artefact of crystal packing, however high level ab initio calculations carried out in our laboratory (B3LYP/6-31G(d)) have determined the binding energy of the HDippForm dimer to be a considerable 46.66 kJ mol^{-1} [57], wherein each HDippForm ligand participates in two hydrogen bonding interactions (as per [(HDippForm)$_2$] in solid-state) [56]. Consequently, the inclusion of HDippForm in the molecular structure of **2** suggests that significant metal interaction of the protonated ligand, in excess of that observed in the solid-state, takes place. Furthermore, the *Z*-conformation of the C–N of the HDippForm in **2** contrasts with the *E*-conformation determined crystallographically for the HDippForm dimer [56], thereby incurring considerable steric strain [58]. Thus, to countenance the inclusion of HDippForm in **2**, and the subsequent disintegration of the polymer of **1**, there must be some energetic recompense. We believe this may be the generation of a [K(DippForm)(HDippForm)] unit in solution. Lastly, the preference for η^6-arene coordination in the solid-state composition **1** (two per Dippform coordinated potassium atom) highlights the affinity of potassium for π-interactions even in the presence of recognised strong Lewis base donors.

3. Experimental

The formamidinate ligand *N*,*N*′-di(2,6-diisopropylphenyl)formamidine, HDippForm, was synthesised according to a modification of a published procedure [37,59]. Potassium bis(trimethylsilyl)amide (0.5 M solution in $C_6H_5CH_3$) was purchased from Aldrich and used as received. Tetrahydrofuran (THF) and C_6H_{14} were dried over Na, freshly distilled from Na–K alloy and freeze-thaw degassed prior to use. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity dinitrogen in flame-dried glassware due to the pronounced aerobic sensitivity of both species. IR spectra were recorded as Nujol mulls using NaCl 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 *deutero*-THF solvent. M.p.s were determined in sealed glass capillaries under dinitrogen and are uncorrected. Due to the lability of solvent, repeated difficulties were encountered in obtaining satisfactory microanalyses for compounds **1** and **2**.

3.1. [{K(η^6:η^1-DippForm)$_2$K(THF)$_2$}$_n$]·*n*THF (**1**)

Potassium bis(trimethylsilyl)amide (2.0 cm^3, 1.00 mmol) was added dropwise to a solution of HDippForm (0.36 g, 0.99 mmol) in THF (25 cm^3). The resulting misty colourless solution was stirred overnight prior to removal of all volatiles in vacuo to yield a light yellow oil. Washing with cold C_6H_{14} (0 °C, ca. 2 × 5 cm^3)

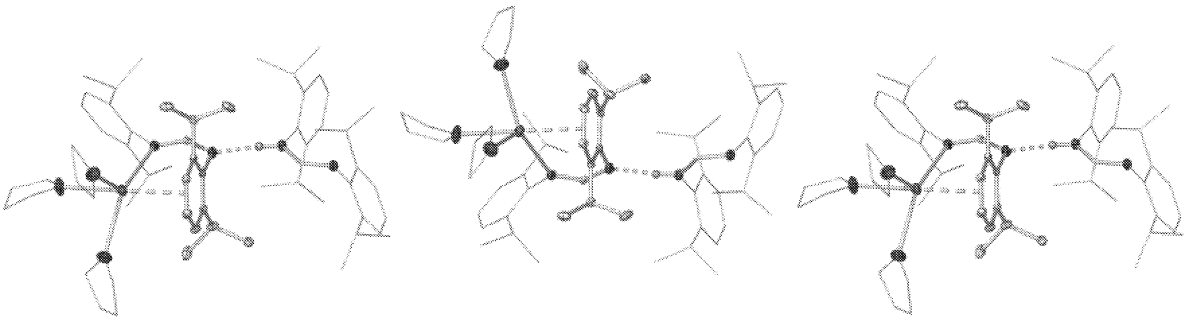

Fig. 3. Supramolecular 'topochemical' arrangement of **2**. All hydrogen atoms except H(1A) are omitted for clarity. Relevant lengths (Å) and angles (°) are not listed in Table 1: N(1A)–H(1A) 0.902, H(1A)···N(2) 1.89(6), N(1A)···N(2) 2.782(6), K(1)–O(1) 2.693(2), K(1)–O(2) 2.700(2), K(1)–O(3) 2.682(2), K(1)···K(1)# 15.753(4), N(1A)–C(25A) 1.343(3), N(2A)–C(25A) 1.267(3), N(1A)–H(1A)···N(2) 171.1, N(1A)–C(25A)–N(2A) 124.3(2), O(1)–K(1)–O(2) 80.97(8), O(1)–K(1)–O(3) 86.83(8), O(2)–K(1)–O(3) 93.52(8), K(1) projection from N(1)O(2)O(3) plane; 0.025 Å.

produced a colourless precipitate that was extracted into THF (ca. 2 cm^3) and placed at −10 °C. This gave the title product as small colourless rods (0.43 g, 85%), m.p. 247 °C (dec.). ^{1}H-NMR (OC_4H_8, 300 K): δ 1.15 (br s, 48H, CH(CH_3)), 1.72 (m, 12H, CH_2 THF), 3.38 (br s, 8H, CH(CH_3)), 3.58 (m, 12H, OCH_2 THF), 7.06 (br s, 12H, Ar–H), 8.86 (br s, 2H, NC(H)N). ^{1}H-NMR (OC_4H_8, 223 K): δ 1.15 (d, 48H, CH(CH_3), [$^3J_{HH}$ 7.1 Hz]), 1.71 (m, 12H, CH_2, THF), 3.38 (septet, 8H, CH(CH_3)$_2$, [$^3J_{HH}$ 7.1 Hz]), 3.57 (m, 12H, OCH_2 THF), 6.59 (m, 4H, η^6-Ar *meta*-H), 6.70 (m, 6H, η^6-Ar *para*-H and non-η^6-Ar *para*-H), 7.05 (m, 2H, non-η^6-Ar *para*-H), 8.93 (s, 2H, NC(H)N). ^{13}C-NMR (OC_4H_8, 300 K): δ 24.3 (s, CH(CH_3)$_2$), 25.5 (s, CH(CH_3)$_2$), 29.0 (s, CH_2 THF), 67.6 (s, OCH_2 THF), 123.7 (s, Ar–C), 128.4 (br s, Ar–C), 125.8 (br s, Ar–C), 139.3 (br s, Ar–C), 163.1 (s, NC(H)N). IR (Nujol, cm^{-1}): ν 757m, 781m, 888m, 845w, 910m, 933m, 1055s, 1140w, 1158m, 1184m, 1234m, 1256m, 1314m, 1345m, 1377, 1460s, 1540s, 1591m, 1665w.

3.2. [K(η^6:η^1-DippForm)(THF)$_3$]·HDippForm (**2**)

A solution of HDippForm (0.10 g, 0.27 mmol) in THF (10 cm^3) was added to a solution of freshly isolated **1** (0.13 g, 0.13 mmol) in THF (15 cm^3). The resulting solution was stirred overnight, concentrated in vacuo (ca. 2 cm^3), and placed at −10 °C. This gave **2** as large colourless prisms (0.19 g, 76%), m.p. 288 °C (dec.). ^{1}H-NMR (OC_4H_8, 300 K): δ 1.18 (br d, 48H, CCH_3, [$^3J_{HH}$ 6.7 Hz]), 1.73 (m, 12H, CH_2, THF), 3.38 (br m, 8H, CH(CH_3)$_2$), 3.62 (m, 12H, OCH_2, THF), 7.08 (br m, 12H, Ar–H), 7.28 (br s, 1H, HDippForm NC(H)N), 8.87 (br s, 1H, NC(H)N), 9.27 (br s, 1H, NC(H)NH). ^{1}H-NMR (OC_4H_8, 223 K): δ 1.13 (br d, 48H, CCH_3, [$^3J_{HH}$ 7.2 Hz]), 1.72 (m, 12H, CH_2, THF), 3.37 (septet, 8H, CH(CH_3)$_2$, [$^3J_{HH}$ 7.2 Hz]), 3.58 (m, 12H, OCH_2, THF), 6.86 (br m, 4H, η^6-Ar *meta*-H), 7.06 (br m, 2H, η^6-Ar *para*-H), 7.15 (br m, 6H, non-η^6-Ar *meta*/*para*-H), 7.56 (br s, 1H, HDippForm NC(H)N), 8.93 (br s, 1H, NC(H)N), 9.23 (br s, 1H, NC(H)NH). ^{13}C-NMR (OC_4H_8, 300 K): δ 24.5 (s, CH(CH_3)$_2$, 29.2 (s, CH(CH_3)$_2$, 30.0 (s, CH_2, THF), 67.6 (s, OCH_2, THF), 123.8 (s, Ar–C), 123.9 (s, Ar–C), 133.7 (s, Ar–C), 139.1 (s, Ar–C), 146.5 (s, HDippForm NC(H)NH), 162.7 (s, DippForm NC(H)N). IR (Nujol, cm^{-1}): ν 761m, 780m, 891m, 856m, 912m, 935w, 1143w, 1161m, 1189m, 1231m, 1260m, 1315s, 1353m, 1360m, 1457s, 1531s, 1547s, 1601m, 1675w, 3106s br.

3.3. X-ray crystallography

Crystalline samples of compounds **1** and **2** were mounted upon glass fibres, in viscous hydrocarbon oil. Crystal data were obtained using an Enraf–Nonius Kappa CCD. X-ray data were processed using the DENZO program [60]. Structural solution and refinement was carried out using the SHELX suite of programs [61] with the graphical interface X-Seed [62]. All hydrogen atoms except H(1A) of **2** were placed in calculated positions (riding model). Hydrogen H(1A) (compound **2**) was found and refined isotropically. For compound **1**, the repeated poor quality of crystalline material, and therefore data, demanded that atoms O(3), C(30), C(31), C(32) and C(33) be refined using an ISOR refinement (0.05) due to pronounced elongation along one polar axis after anisotropic refinement. Also, one coordinated THF ligand of **1** resides upon a mirror plane (O(1) ligand) and is necessarily disordered over two sites of equal occupancy, and one set of isopropyl groups (C24) are disordered over two sites. The latter were successfully modelled with ca. 47:53% occupancy (C(24A) and C(24B), respectively). Crystal data and refinement parameters for all complexes are compiled below.

3.3.1. Crystal data for **1**

$C_{31}H_{47}KN_2O_{1.50}$, $M = 510.81$, colourless small rods, $0.20 \times 0.10 \times 0.10$ mm, monoclinic, space group $P2_1/m$ (No. 11), $a = 10.804(2)$, $b = 26.265(5)$, $c = 11.812(2)$ Å, $\beta = 115.32(3)°$, $V = 3030.0(11)$ Å^3, $Z = 4$, $D_{calc} = 1.120$ g cm^{-3}, $F(000) = 1112$, Nonius Kappa CCD, Mo–K_α radiation, $\lambda = 0.71073$ Å, $T = 123(2)$ K, $2\theta_{max} = 56.7°$,

28 163 reflections collected, 7554 unique ($R_{int} = 0.1724$). Final goodness-of-fit = 0.941, $R_1 = 0.0964$, $wR_2 = 0.2187$, R indices based on 2378 reflections with $I > 2\sigma(I)$ (refinement on F^2), 361 parameters, 30 restraints. Lp and absorption corrections applied, $\mu = 0.201$ mm^{-1}.

3.3.2. Crystal data for **2**

$C_{62}H_{95}KN_4O_3$, $M = 983.52$, colourless large prisms, $0.30 \times 0.25 \times 0.20$ mm, monoclinic, space group $P2_1/n$ (No. 14), $a = 17.439(4)$, $b = 17.194(3)$, $c = 21.144(4)$ Å, $\beta = 107.38(3)^\circ$, $V = 6051(2)$ Å^3, $Z = 4$, $D_{calc} = 1.080$ g cm^{-3}, $F(000) = 2152$, Nonius Kappa CCD, Mo–K$_\alpha$ radiation, $\lambda = 0.71073$ Å, $T = 123(2)$ K, $2\theta_{max} = 56.6^\circ$, 64 060 reflections collected, 14 894 unique ($R_{int} = 0.1143$). Final goodness-of-fit = 0.907, $R_1 = 0.0699$, $wR_2 = 0.1513$, R indices based on 5655 reflections with $I > 2\sigma(I)$ (refinement on F^2), 651 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.132$ mm^{-1}.

4. Conclusion

We have demonstrated that the potassium metallation of *N*,*N*′-di(2,6-diisopropylphenyl)formamidine resembles that of *N*,*N*′-di(mesityl)formamidine, HDMesForm. The significant increase in steric bulk of DippForm frustrates the formation of [K(formamidinate)(formamidine)] units. For DMesForm, these are chemically inert in the presence of [K{N(SiMe$_3$)$_2$}] and strong Lewis base donors. To rationalise this, it appears the 2,6-isopropyl groups of DippForm diminish metal–ligand proximity (see Table 1). In solution, both **1** and **2** display fluxional potassium environments that have been studied by ^{1}H-NMR. The DippForm coordination of both represent the second/third incidence of η^6:η^1-binding for *N*,*N*′-di(aryl)amidinates. Thus far, this motif is unique to bulky formamidinate complexes of potassium, the steric bulk frustrating the K(μ_2:η^2:η^2-amidinate)$_2$ archetype of sterically 'slight' amidinate complexes. Macromolecularly, the solid-state structure of **1** forms a one-dimensional polymer, whilst that of **2** suggests a 'topochemically' arranged matrix of [K(DippForm)(THF)$_3$]·HDippForm units. The latter may result from a [K(DippForm)(HDippForm)] composition in solution.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 190477 and 190478 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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(c) η^1:η^1-Unsymmetrical diazaallyl e.g. [Ta(CH_3)Cl_2{(C_6H_{11})NC-(CH_3)N(C_6H_{11})}$_2$]: M.G.B. Drew, J.D. Wilkins, J. Chem. Soc. Dalton Trans. (1974) 1973;
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