Alkali-metal bis(aryl)formamidinates: a study of coordinative versatility

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The development of alkali-metal amidinate reagents, in particular formamidinates, has proceeded hand-in-hand with fundamental advances in transition-metal bonding, *e.g.* metal–metal bonding, and the progressive departure from cyclopentadienyl support ligands in early transition-metal catalysis. This highly personalised account highlights the coordinative versatility of one alkali-metal amidinate subclass; the bis(aryl)formamidinates. These compounds have proven invaluable during transition-metal studies but were considered unworthy of investigation in their own right prior to our work.

Introduction

Neutral amidines† and guanidines have found themselves a niche as support ligands in inorganic chemistry and this area has been recently reviewed.[1] Deprotonated amidines and guanidines, *viz.* amidinates and guanidinates (Fig. 1), have also found great utility in this regard and several excellent reviews have appeared covering the chemistry of amidinate ligands,[2] benzamidinates and other heteroallylic ligands as supports for lanthanoid metals,[3] *N*-silylated benzamidinates in main group and coordination chemistry,[4] and the coordination chemistry of guanidines and guanidinates.[5] Absent in this area is an overview of the alkali-metal chemistry of bis(aryl)formamidinate ligands (Fig. 1), an area in which we have been active for the past five years.

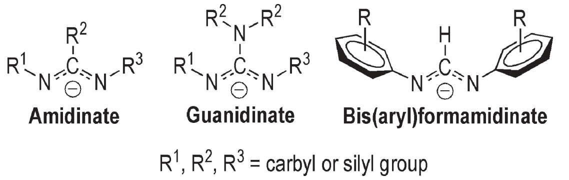

Fig. 1 Basic ligand frameworks for amidinate, guanidinate and bis(aryl)formamidinates.

Our interest in bis(aryl)formamidinates stems from our application of bulky variants of these ligands to kinetically stabilise group 13 hydride complexes,[6] sterically engineer carbon–fluorine bond activation[7] or act as anionic ligand supports for group 2[8] and low valent compounds.[7b,9] Since these applications necessitate an intimate understanding of metal–amidinate coordination, we developed a strong interest in the coordination modes exhibited by these compounds particularly in the solid state. It is well-established that there are structure–reactivity relationships for many alkali-metal organometallics and organoamidometallic species,[10] and we

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† By amidine and amidinate we refer to 1,2,3-trisubstituted 1,3-diazaallyl species, as per Fig. 1, throughout this article.

Peter Junk

Peter Junk is a graduate of The University of Western Australia where he completed both his BSc (Hons) (1984) and PhD (1988) degrees under the supervision of Prof. Colin Raston. After four years employed in the petroleum industry, Peter undertook postdoctoral research with Prof. Jerry Atwood (University of Alabama), Prof. Allan White (University of Western Australia) and Prof. Glen Deacon (Monash University) before being appointed to a lectureship at James Cook University in 1997. In 2001 he moved to Monash University and was given accelerated promotion to Associate Professor in 2003 and to his current position of Professor in 2007. His research interests span the inorganic and organometallic chemistry of the main group and lanthanoid elements.

Marcus Cole

Marcus Cole was born in Northampton, England, in 1976. He completed both his BSc (Hons) (1998) and PhD (2001) degrees at Cardiff University, UK, the latter working on The Stabilisation and Reactivity of Indium Hydride Complexes under the supervision of Prof. Cameron Jones. He then moved to a Royal Society Postdoctoral Fellowship (2002) and ARC Research Fellowship (2003) at Monash University working on s- and f-block organoamide chemistry in conjunction with Assoc. Prof. Peter C. Junk. In early 2004 he was appointed to a lectureship at the University of Adelaide where his research interests include synthetic applications of group 2, 3 and 13 hydride compounds and low valent complexes supported by organoamide ligands.

believed a similar study of bis(aryl)formamidinates would prove useful to their broad application, especially as most are prepared and used *in-situ* during salt-elimination syntheses. When we began our foray into this chemistry, there was a single structurally authenticated alkali-metal bis(aryl)formamidinate[11] (*cf.* > 250 reported transition-metal species).[12] In the article describing this compound it was stated that "…this is the first time a crystal structure has been determined on a lithium amidinato compound in spite of the fact that these compounds are so widely used in the preparation of transition-metal amidinato complexes. The reason for the lack of crystal structure determinations is probably the facility which the crystals lose ether." It is the intention of this article to highlight the development of alkali-metal bis(aryl)formamidinates in the nine years since this report and to emphasise the considerable coordinative versatility of this family of ligands which, thus far, has only been touched upon.

Amidines and advances in transition-metal chemistry

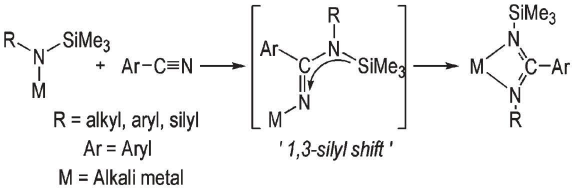
Amidinates may be introduced to a metal coordination sphere using a variety of synthetic routes.[2] A brief survey of amidinate chemistry over the past fifty years indicates that three paths, **1**–**3** (see below for examples), have become particularly prominent in transition-metal chemistry. These comprise salt-elimination route **1**,[13] which requires a suitable metal halide/acetate precursor, oxidative decarbonylation path **2**,[14] which is typically accompanied by H_2 evolution as a redox by-product, and hydrocarbon elimination route **3**,[15] which necessitates handling of an air-sensitive metal alkyl. Of these, route **1** has become particularly important.[2–4] This path requires an alkali metal (or other suitable metal) amidinate and it could be argued that the commercial availability of alkali-metal alkyls and amides as alkali-metal amidinate precursors, and concurrent unavailability of favoured amidinates, *e.g.* $[Me_3SiNC(Ph)NSiMe_3]^-$ pioneered by Roesky, Dehnicke and Edelmann (Scheme 1),[2–4] as their neutral amidines, has prejudiced the field towards path **1**.

$$[VCl_3(THF)_3] + 2\,[Li\{CPh(NSiMe_3)_2\}] \rightarrow [VCl\{CPh(NSiMe_3)_2\}_2(THF)] + 2\,LiCl \qquad (1)$$

$$2\,[Cr(CO)_6] + 4\,(4\text{-}MeC_6H_4)NC(H)NH(4\text{-}MeC_6H_4) \rightarrow [Cr_2\{CH(N(4\text{-}MeC_6H_4))_2\}_4] + 2\,H_2 + 12\,CO \qquad (2)$$

$$[ZnEt_2] + 2\,PhNC(Ph)NHPh \rightarrow [\{Zn(CH(NPh)_2)_2\}] + 2\,EtH \qquad (3)$$

Unlike some amidine and guanidine counterparts the conventional precursors to bis(aryl)formamidinates are neutral bis(aryl)formamidines. Although metal hydride addition across a disubstituted 1,3-carbodiimide should not be dismissed as an alternative synthesis,[6b,16] the archetypal means of synthesising bis(aryl)formamidines is the condensation of two equivalents of a substituted aniline with one equivalent of triethylorthoformate (**4**). Historically, the availability of neutral amidines such as *N*,*N′*-diphenylbenzamidine (PhNC(Ph)NHPh) led transition-metal researchers toward synthetic path **2**.[2] Indeed, the first documented synthesis of a transition-metal amidinate, reported in 1975 by Cotton and Kilner,[17] comprised the oxidative decarbonylation of $[Mo(CO)_6]$ with *N*,*N′*-diphenylbenzamidine to yield the quadruply bonded 'paddlewheel' complex $[Mo_2\{C(Ph)(NPh)_2\}_4]$. The simplicity of this preparation and the free availability of neutral bis(aryl)formamidines rapidly led to their introduction to this field with the preparation of $[M_2$(bis(aryl)formamidinate)$_4]$ chromium and molybdenum complexes by de Roode and Vrieze in 1977.[14] Combined with earlier isoelectronic carboxylato complexes,[18] the resulting studies have been critical to our understanding of multiply bonded metal–metal complexes. It is fair to say that today this family of ligands and their alkali-metal salts are a key component of this research area, as evidenced by the 367 structurally authenticated complexes containing a transition metal–metal bond bridged by an bis(aryl)formamidinate, of which 121 are solely bridged by four such ligands.[12]



Scheme 1 Reaction pathway for typical preparation of alkali-metal *N*-silyl benzamidinate species.

$$CH(OEt)_3 + 2\,NH_2Ar \rightarrow ArNC(H)NHAr + 3\,EtOH\ (Ar = aryl) \qquad (4)$$

The modern development of organometallic chemistry has also seen amidinates come to the fore as support ligands in homogeneous catalysis.[1,2] This field has traditionally relied on cyclopentadienyl (Cp) and phosphane ligands as anionic and neutral ligands respectively, and the steric and electronic modification of these has been crucial to catalyst development. However, for some applications, especially those where π-acceptor ligands are not paramount, it has become evident that 'Cp' ligands do not offer enough steric flexibility and control. This has initiated a move toward metal organoamide species particularly for early transition-metal catalysis.[19] Applications in this regard include living olefin polymerisation,[20] nitrogen fixation[21] and C–H activation.[22] The easy accessibility of alkali-metal silyl substituted benzamidinates (*vide supra*) from the reaction of silyl substituted alkali-metal metal amides with aryl nitriles followed by a 1,3-silyl shift (Scheme 1),[4] has led to numerous amidinate applications that borrow principles and methodology learnt from metallocene chemistry.[19] In doing so amidinates, including bis(aryl)formamidinates, have availed themselves well amongst organocarbides due to their flexibility, which offers a bounty of coordination modes (*vide infra*), and ease of synthesis, placing them very much at the fore of the organoamide drive in early transition-metal chemistry.

Amidinate binding modes

Several spectroscopic tools may be used to discern the mode of coordination for a metal amidinate complex.[2] To this end, many infrared and NMR spectroscopic studies of amidinate binding are documented in the literature.[23] The use of these methods is complicated significantly when more than one binding mode is present and/or the complex exhibits fluxional coordination in solution. Indeed, with few exceptions, NMR studies have centred on solution state binding mode fluxionality. These studies, which may not have been attempted without binding mode information obtained from crystallographic data, rely on variable temperature NMR spectroscopy. Infrared spectra tethered to structural data provide the most revealing binding-spectroscopic trends. These have been extensively catalogued by Barker and Kilner[2] using the available reported examples prior to 1994 and can be roughly summarised, as per the formamidinate studies of Vrieze and co-workers,[23] as monodentate amidinates (see Fig. 2, **I**) exhibit characteristic IR absorptions at *ca.* 1200, 1310, 1550 and 1610 cm^{-1}, chelating amidinates (Fig. 2, **II**) at 1560, 1620 and 1645 cm^{-1}, and bridging bimetallic amidinates (Fig. 2, **III**) at *ca.* 1480, 1560, 1590 and 1610 cm^{-1}. These values are useful as a guide to likely binding modes, but vary considerably with nuances in the bonding and, as listed previously, cannot be used as an effective binding mode diagnosis for systems that display multiple binding modes. Accordingly, X-ray structure determination and related diffraction techniques represent the contemporary methods of choice for unequivocal identification of binding mode.

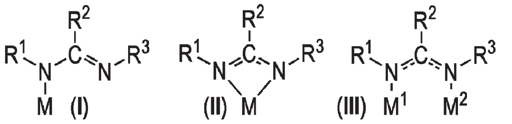


Fig. 2 Typical binding modes employed by mono- and dinuclear metal amidinate complexes.

A survey of the Cambridge structural database indicates that amidinates can coordinate metals by a range of bonding modes. These modes may be classified by the isomeric form of the amidinate as *E-syn, E-anti, Z-syn or Z-anti* (see Fig. 3),[24] with *Z-syn* highly unlikely due to buttressing of *N*-substituents, and then separated into broad classes that, non-NCN diazaallyl coordination aside *e.g.* pendant donors, rely on either two or four electron nitrogen σ-donation (see Fig. 2, all depicted with *E-anti* amidinate): monodentate **I**, bidentate chelating **II** and bimetallic bridging **III**. Of these, the four-electron donor-modes **II** and **III** are the most common, **II** being the expected coordination when **III** is not sterically or electronically favoured. Classic examples of this are the aforementioned metal–metal bonded paddle-wheel complexes pioneered by Cotton,[17,18] Murillo,[25] Bear,[26] Ren[27] and co-workers. By comparison, examples of **I**, which typically require significant 'ML_n' or amidinate steric bulk[28] or a preferred pendant donor, are scarce.

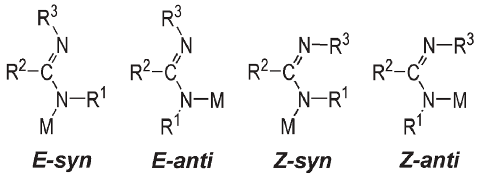


Fig. 3 Possible isomeric forms for amidinates in metal amidinate complexes.[24]

Several modifications of all three classes are possible. These binding subclasses either arise from variation in electron localisation within the anionic NCN backbone of **II** or from increased metal–ligand interactions in **III**. For instance, the nitrogen donors of a symmetrically substituted charge delocalised amidinate can interact equally with the chelated metal centre to give M–N bond lengths and amidinate backbone C–N bond lengths representative of a conjugated donor (**II**).[29] However, if charge localisation at one nitrogen is favoured, discrete C–N and C=N bonds result across the amidinate. In this instance, aside from monodentate coordination type **I**, two types of four-electron donation are possible (see **IV** and **V**, Fig. 4). The first, **IV**, requires imine *N*-electron pair donation. Unlike **II**, this bonding mode is accompanied by distinct differences in M–N and backbone C–N bond lengths.[30] The second *electron localised* donor type, **V**, replaces imino *N*-donation by imino C=N π-donation.[31]

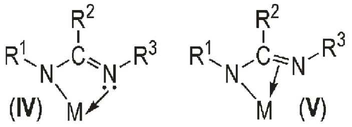


Fig. 4 Possible modifications of binding mode **II**.

Without invoking non-NCN donor interactions, the remaining binding subclasses are simply variations of bridging dinuclear mode **III** and higher nuclearity species. Tri- and tetranuclear bridging amidinates aside, these are the bridging–chelating modes **VI**[32] and **VII**.[33] Both are accompanied by a twisting of the NCN donor plane to orthogonal relative to the intermetallic vector (Fig. 5).

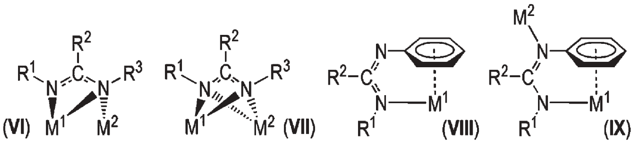


Fig. 5 Increased metal–ligand *N*-donor variants of binding mode **III** and *N*,*Aryl*-coordination modes **VIII** and **IX**.

The final mono- or dinuclear amidinate coordination subclasses are a variant of **I** that necessitate a *Z-anti* amidinate with an *N*-aryl substituent (= R^3) whereby the aryl group coordinates to permit chelation (**VIII**) of the metal (Fig. 5).[34] This mode can occur with varying metal–arene hapticities (η^1–η^6) and may be accompanied by a bridging interaction to a second metal using the nitrogen of the aryl donor (**IX**).[35]

There are thirteen complexes that exhibit amidinates coordinated concurrently to three[36] or four[37] separate metal centres. The binding modes exhibited by these species can be expressed as a combination of two mononuclear, *i.e.* **I**, **II**, **IV** or **V**, or dinuclear, *i.e.* **III**, **VI** or **VII**, *N*-coordination modes that each have exclusive metals (see Figs. 2–5). The modes with literature precedent are illustrated in Fig. 6. The complex $[\mathrm{Os_3(\mu\text{-}H)\{CH(NCH_3)_2\}(CO)_9}]$[36e] (see Fig. 6) is the only non-alkali metal complex of the thirteen species.

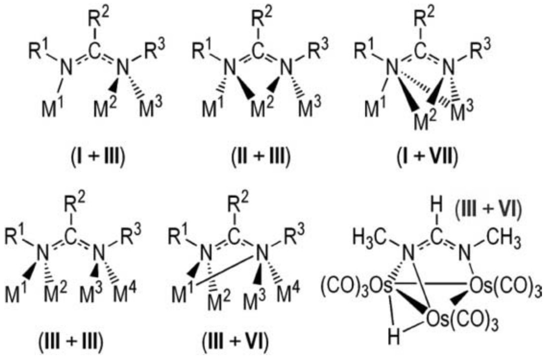


Fig. 6 Tri- and tetranuclear amidinate bridging binding modes and $[\mathrm{Os_3(\mu\text{-}H)\{CH(NCH_3)_2\}(CO)_9}]$ illustrating **I + III** mode.[36e]

While the bonding modes **I–IX** have precedent in the structural catalogue, only the chelating mode **II**, its asymmetric variant **IV**, and bridging mode **III** can be said to be common. There are greater than 450, 100 and 600 documented examples of each respectively.[12] This contrasts the fewer than twenty examples of bonding type **I** (see Fig. 7 for example).[28a] Complexes exhibiting the increased metal–ligand bonding bridging modes **VI** and **VII** have become more prominent in recent times with 32 and 23 examples, respectively (Fig. 5).[12] Furthermore, examples of bonding modes **V**, **VIII** and **IX** are limited to less than ten examples each, of which only the mercury compounds $[\mathrm{Hg\{Me_3SiNC(Ph)NR\}_2}]$ (**V**) (R = $\mathrm{SiMe_3}$ or $\mathrm{C(Ph){=}C(SiMe_3)_2}$)[38] and low valent group 13 species $[\mathrm{M(DippNC(^tBu)NDipp)}]$[39] (**VIII**) (M = In, Tl; Dipp = 2,6-diisopropylphenyl) do not contain an alkali metal (Fig. 7). Indeed, the variation of amidinate coordination observed when using alkali metals appears to exceed that of all other groups in the periodic table. Beyond this trend, it is also apparent that bis(aryl)formamidinates of lithium, sodium and potassium display significantly greater structural variation than other amidinate subclasses (*vide infra*). Similar variation is expected for rubidium and caesium, although this area is yet to be studied either in solution or the solid state. Such versatility arises from the decreased steric bulk of hydrogen at the NCN donor unit carbon. This permits opening and closing of the NCN bite and ready adaptation of the donor set to the metal at hand. A consequence of this is that these ligands can exhibit all nine of the aforementioned mono- and dinuclear bonding modes and several of those in the tri- and tetranuclear category. To our knowledge, the bis(aryl)formamidinates are the only ligand class that can claim this feat.

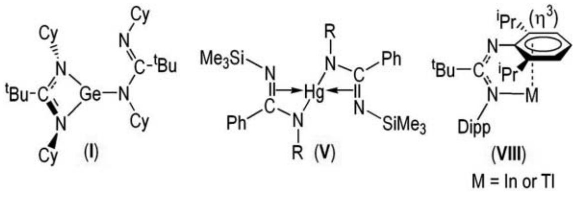
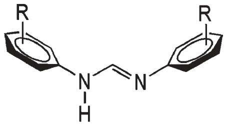


Fig. 7 Literature examples of metal amidinates exhibiting binding modes **I**,[28a] **V**,[38] and **VIII**.[39]

For the purpose of brevity, the bis(aryl)formamidinates in this article have been referred to throughout using an abbreviated title. Refer to Scheme 2 for a full list of abbreviations.



R =	Abbreviation
o-Me	oTolFormH
m-Me	mTolFormH
p-Me	pTolFormH
2,6-Me$_2$	DimpFormH
2,4,6-Me$_3$	MesFormH
2,6-Et$_2$	DiepFormH
2,6-^{i}Pr$_2$	DippFormH
o-F	oMfpFormH

Scheme 2 List of abbreviations used for bis(aryl)formamidinates featured in this article.

Lithium complexes

The deprotonation of bis(aryl)formamidines can be effected using *n*-BuLi (see Table 1 for a full list of lithium compounds described in this article). This high yielding reaction is typically performed in donor solvents such as THF, 1,2-dimethoxyethane (DME) and $\mathrm{Et_2O}$ or in the presence of a chelating amine such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) or *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA). So far, we have not studied these species in the absence of a coordinating solvent or amine, firstly because of compound insolubility and secondly because the *in situ* preparation and use of these compounds occurs in such solvents[2,11] making the structure, nuclearity and NCN coordination of these species of great importance during reactivity.

For preparations performed in THF, the steric bulk of the formamidinate ligand generates great variety in amidinate binding. In reactions involving the least sterically demanding ligand at our disposal; pTolFormH, a dinuclear complex is obtained (Fig. 8).[36a] In this compound, the amidinate ligands bridge the lithium centres by class **III** coordination accompanied by bridging by a single THF donor. A similar structure was obtained using MesForm despite the increased steric bulk of the ligand.[40] For oMfpForm, where the steric bulk of the ligand is presumably intermediate to pTolForm and MesForm (size of $\mathrm{CH_3} \approx \mathrm{F}$), the availability of *ortho*-fluoride donors leads to a greater lithium–lithium separation and excludes the bridging THF donor of the pTolForm and MesForm species (Fig. 9).[36d] Increasing the steric hindrance even further by incorporation of ethyl groups at the 2,6-aryl positions (DiepForm) produces a compound with empirical composition identical to that of the pTolForm and DimpForm species above, however this belies a new structural motif (Fig. 10), *viz*. a four-coordinate lithium atom chelated by two formamidinate ligands, one *E-anti* *N*,*N*′-donor (**II**) and one *Z-anti* *N*,*C*-donor (**VIII**, η^1), with a $\mathrm{Li(THF)_3}$ unit coordinated to the *Z-anti*

Table 1 Summary of the binding modes, nuclearity and composition of lithium compounds described in this article

Ligand	Solvent	Formula	Nuclearity	Binding mode[a]	Comments
pTolForm	THF	$[Li_2(pTolForm)_2(\mu\text{-}THF)(THF)_2]$	2	**III**	Unusual bridging THF ligand.
DimpForm	THF	$[Li_2(DimpForm)_2(\mu\text{-}THF)(THF)_2]$	2	**III**	Unusual bridging THF ligand.
oMfpForm	THF	$[\{Li(oMfpForm)(THF)\}_2]$	2	**III**	One fluorine of each oMfpForm coordinates to a lithium.
DiepForm	THF	$[Li(THF)_3Li(DiepForm)_2]$	2	**II** and **IX**	One lithium coordinated by both a type **VIII** (η^1) and type **II** ligand.
DippForm	THF	$[Li(DippForm)(THF)_2]$	1	**II**	
pTolForm	DME	$[Li(DME)_3][Li_2(pTolForm)_3]$	Ionic	**III**	Ionic, dinuclear anion.
oTolForm	DME	$[Li(DME)_3][Li(oTolForm)_2]$	Ionic	**II**	Ionic, mononuclear anion.
MesForm	DME	$[\{Li(MesForm)(DME)\}_2]$	2	**III**	
DiepForm	DME	$[\{Li(DiepForm)(DME)\}_2]$	2	**III**	
DippForm	DME	$[Li(DippForm)(DME)]$	1	**II**	
pTolForm	TMEDA	$[\{Li_2(pTolForm)_2(\mu\text{-}TMEDA)\}_n]$	Polymer	**VI**	Bridging TMEDA ligand links dinuclear units into polymer.
MesForm	TMEDA	$[Li(MesForm)(TMEDA)]$	1	**II**	First monomeric alkali-metal formamidinate reported.
DimpForm	PMDETA	$[Li(DimpForm)(PMDETA)]$	1	**I** and **V**	Both binding modes present in molecular structure.
DiepForm	PMDETA	$[Li(DiepForm)(PMDETA)]$	1	**I**	
DippForm	PMDETA	$[Li(DippForm)(PMDETA)]$	1	**V**	

[a] See Fig. 2 and 4–6 for illustration of binding modes.

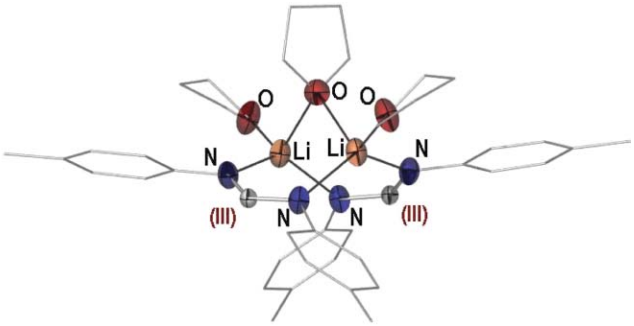


Fig. 8 Molecular structure of $[Li_2(pTolForm)_2(\mu\text{-}THF)(THF)_2]$ (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and hydrocarbyl groups depicted as wireframes.

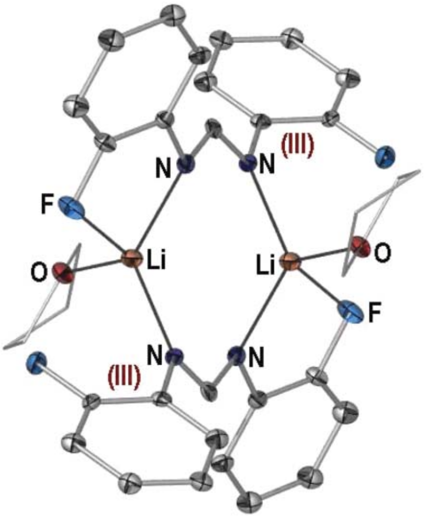


Fig. 9 Molecular structure of $[\{Li(oMfpForm)(THF)\}_2]$ (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and THF hydrocarbyl groups depicted as wireframes.

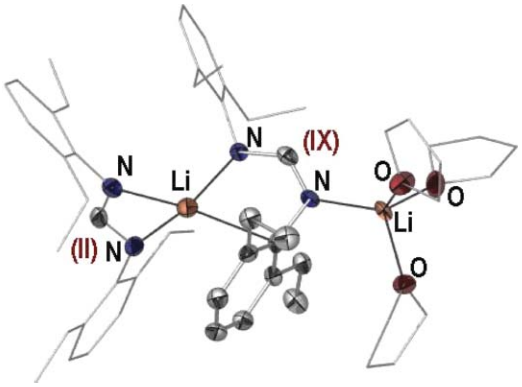


Fig. 10 Molecular structure of $[Li(THF)_3Li(DiepForm)_2]$ (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and hydrocarbyl groups depicted as wireframes.

ligand (**IX**) by nitrogen donation *exo* to the $Li(DiepForm)_2$ unit.[41] This compound represents the limit of dinuclearity for lithium–THF species, whereby a progression to DippForm results in a mononuclear compound with a chelating class **II** amidinate and two terminal THF ligands.[41] Thus, while the coordination number of the lithium atoms (four-coordinate) does not change throughout the series; remarkable structural variation does arise.

A simple change of the supporting solvent has a dramatic influence on the structures of the resulting complexes. Replacement of THF with DME gives rise to entirely new alkali-metal formamidinate coordination modes. In the cases of both *ortho*- and *para*-methyl substituted phenyl formamidinates, pTolForm and oTolForm, respectively, closely related ionic structures containing the octahedral $[Li(DME)_3]^+$ cation are obtained. In the former, a dinuclear solvent-free anion $[Li_2(pTolForm)_3]^-$ (Fig. 11) with three type **III** ligands is obtained,[36a] while for the latter a mononuclear anion $[Li(oTolForm)_2]^-$ with a distorted tetrahedral (two chelating type **II** ligands) lithium is obtained.[40] A move to the

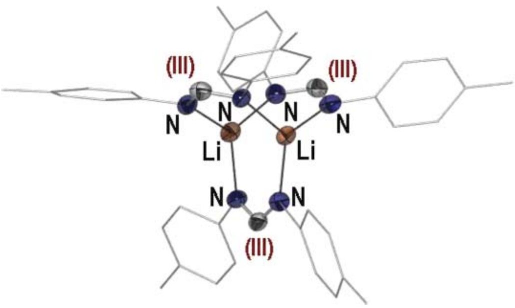


Fig. 11 Molecular structure of anion of [Li(DME)$_3$][Li$_2$(pTolForm)$_3$] (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and hydrocarbyl groups depicted as wireframes.

di(2,6-dialkylphenyl)formamidinates provides *classic* dimer structures for both DimpForm and Diepform, with bridging type **III** ligands and chelation by a single DME ligand (Fig. 12).[41] The transition from di- to mononuclear species occurs with the use of DippForm.[41] This generates a complex with a type **II** ligand accompanied by a chelating DME to give a four-coordinate monomer.

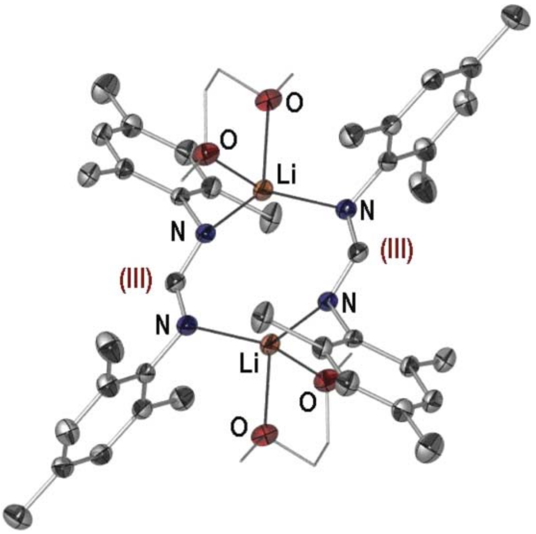


Fig. 12 Molecular structure of [{Li(MesForm)(DME)}$_2$] (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and DME hydrocarbyl groups depicted as wireframes.

The incorporation of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) and tridentate *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) into lithium bis(aryl)formamidinate chemistry provided unique *N*-donor binding modes. In [Li$_2$(pTolForm)$_2$(TMEDA)]$_n$ a polymeric complex is formed using the typically chelating TMEDA ligand as a bridge between successive [Li$_2$(pTolForm)$_2$] (**VI**) units (Fig. 13).[36a] Mononuclear structures are obtained for [Li(MesForm)(TMEDA)], [Li(DimpForm)(PMDETA)], [Li(DiepForm)(PMDETA)] and [Li(DippForm)(PMDETA)] with distinct structural variations between all four. [Li(MesForm)(TMEDA)] was the first reported monomeric alkali-metal formamidinate.[40] It was also the first to exhibit a type **II** formamidinate donor. The PMDETA compounds [Li(DimpForm)(PMDETA)], [Li(DiepForm)(PMDETA)] and [Li(DippForm)(PMDETA)] comprise a Li(PMDETA) centre coordinated by a sterically demanding formamidinate in either the *E-syn* or *E-anti* isomeric form.[42] All three exhibit a formamidinate that coordinates in a unique (for Li formamidinate chemistry) η^1-fashion. For the DiepForm species this provides type **I** coordination, however the structures of the DippForm analogue (Fig. 14) and one unique molecule in the asymmetric unit of [Li(DimpForm)(PMDETA)] are indicative of type **V** coordination, which is further evidenced by a decrease in the C–N IR stretching frequency for these species relative to the DiepForm analogue. A comparison of the bonding parameters within [Li(DippForm)(PMDETA)] and a complex exhibiting a type **II** bis(aryl)formamidinate such as [Li(DippForm)(THF)$_2$][41] (Fig. 15) highlights the modification in Li–N bond length(s), closing of the N–Li–N angle and

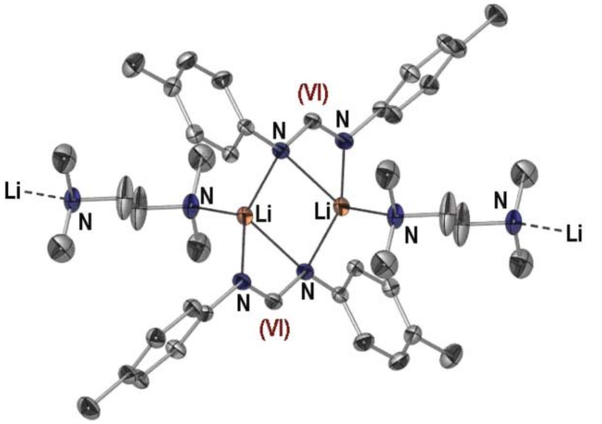


Fig. 13 Molecular structure of repeating unit of [{Li$_2$(pTolForm)$_2$-(μ-TMEDA)}$_n$] (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity.

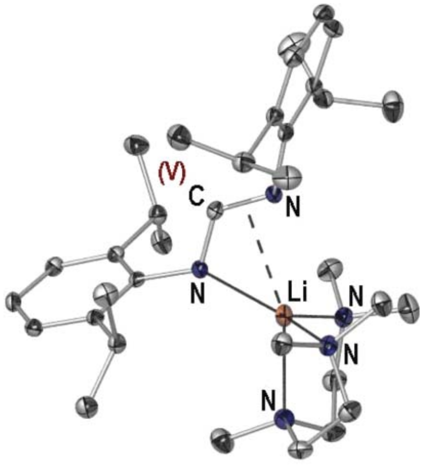


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Fig. 14 Molecular structure of [Li(DippForm)(PMDETA)] (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding mode in parentheses. Hydrogen atoms omitted for clarity.

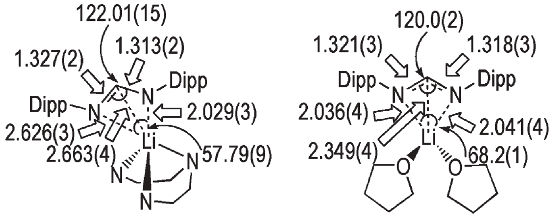

Fig. 15 Diagram illustrating atomic contact (Å) and angle (°) differences between [Li(DippForm)(PMDETA)] and [Li(DippForm)$(THF)_2$]. PMDETA methyl groups omitted and contacts represented as hatched lines.

opening of the NCN bite that typifies this rare coordination mode.[43]

Sodium complexes

The extensive study of lithium organoamide chemistry is extensive relative to that of sodium species.[10] The known alkali-metal amidinates are no exception. This takes particular importance when one considers the increasing number of lithium and/or potassium diazaallylic species reported without consideration of the related sodium reagent. This is presumably due to limited synthetic advantage over an easier to handle lithium analogue[44] or the increased insolubility of potassium halide by-products relative to sodium halides, which typically assists reaction work-up. Indeed, the incorporation of lithium halides is a prominent feature within highly polar electropositive metal organoamide and amidinate/guanidinate systems.[45] In spite of this trend, the enhanced polarity of the sodium–amide bond *viz.* lithium–amide bonds and the increased ionic radius of sodium (Li = 0.76 Å, Na = 1.02 Å)[46] provide ample scope for varied binding interactions when coordinated to bis(aryl)formamidinates. These include rare metal–aryl contacts or increased metal–*N* bridging.

In the following chemistry the ligands were deprotonated using sodium bis(trimethylsilyl)amide, although we have also used sodium hydride on occasion.[36a] We prefer use of the former as it is much easier to stoichiometrically control and we have found the purity of commercial NaH to be of a variable nature. See Table 2 for a full list of sodium compounds described in this article.

Isolation of sodium bis(aryl)formamidinates from THF gives three distinct structure types. For pTolFormH; the trinuclear species $[Na_3(pTolForm)_3(THF)_4]$ results,[36a] in which two of the sodium centres are chelated and bridged by one **VII**-type ligand with further bridging to a third sodium, which is doubly chelated (type **II** ligands) by two formamidinates that also coordinate the former two sodium atoms in a type **III** manner (Fig. 16, see Fig. 6 for **II + III** binding). In $[Na(DiepForm)(THF)]_n$, which resembles its lithium analogue (Fig. 10), the sodium atoms are bound by one *N*-donor atom and an aromatic group of the formamidinate ligand (**VIII**).[41] A one-dimensional polymer is generated by *N*-donation (**IX**) to another sodium atom, itself coordinated by a type **VIII** amidinate, employing the aryl donor nitrogen. The sodium coordination sphere is completed by a terminal THF molecule.

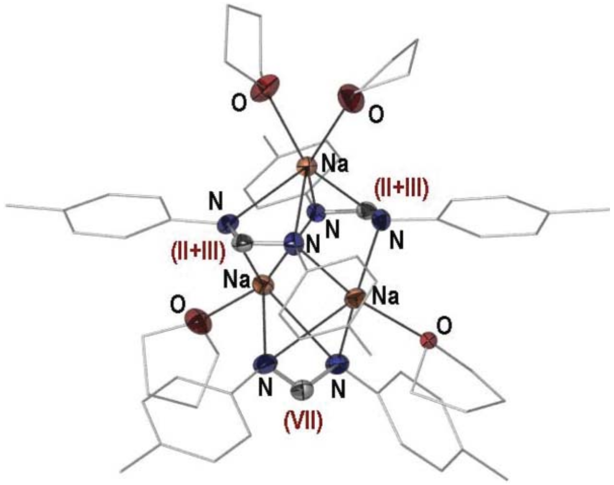

Fig. 16 Molecular structure of $[Na_3(pTolForm)_3(THF)_4]$ (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and hydrocarbyl groups depicted as wireframes.

Table 2 Summary of the binding modes, nuclearity and composition of sodium compounds described in this article

Ligand	Solvent	Formula	Nuclearity	Binding mode[a]	Comments
pTolForm	THF	$[Na_3(pTolForm)_3(THF)_4]$	3	**II + III** and **VII**	Two ligands coordinate across two faces of Na_3 unit by a composite of **II** and **III** type modes.
DiepForm	THF	$[\{Na(DiepForm)(THF)\}_2]$	Polymer	**IX**	Polymer generated by type **IX** ligand (η^6).
DippForm	THF	$[Na(DippForm)(THF)_3]$	1	**II**	
pTolForm	DME	$[\{Na(pTolForm)(DME)\}_2]$	2	**VI**	Analogous to lithium compound with greater formamidinate bridging.
DimpForm	DME	$[Na(DimpForm)(DME)_2]$	1	**II**	
DiepForm	DME	$[\{Na(DiepForm)(DME)\}_2]$	2	**VI**	Unusual structural incontinuity. Decreased DME content and increased nuclearity re: Dimp- and DippForm counterparts.
DippForm	DME	$[Na(DippForm)(DME)_2]$	1	**II**	
oMfpForm	Et_2O	$[\{Na(oMfpForm)(Et_2O)\}_2]$	2	**VI**	Analogous to lithium compound with greater formamidinate bridging. Obtained at low temperature to avoid C–F activation.
oMfpForm	Et_2O	$[\{Na_3(oMfpForm)_3(\mu\text{-}Et_2O)NaF\}_2]$	8	**II + III**	Six formamidinates engage in similar composite **II**/**III** bridging to pTolForm/THF compound. Compound obtained at room temperature.

[a] See Fig. 2 and 4–6 for illustration of binding modes.

It is interesting to note that this compound displays η^6-arene coordination in preference to increased solvent donation. Increasing the steric bulk of the formamidinate ligand to DippForm results in a mononuclear species, *viz.* [Na(DippForm)(THF)$_3$], where the ligand chelates the metal centre (**II**).[41]

Isolation of sodium formamidinates from DME generates either classic **VI**-bridged dimers; *e.g.* [Na$_2$(pTolForm)$_2$(DME)$_2$][36a] (Fig. 17) and [Na$_2$(DiepForm)$_2$(DME)$_2$],[41] or mononuclear species (**II**); *e.g.* [Na(DimpForm)(DME)$_2$] and [Na(DippForm)(DME)$_2$].[41] It is not surprising that a mononuclear species is obtained for the sterically demanding DippForm ligand but, as a dimer is obtained for DiepForm, it is surprising that a dimer is not obtained for the less sterically hindered DimpForm analogue.

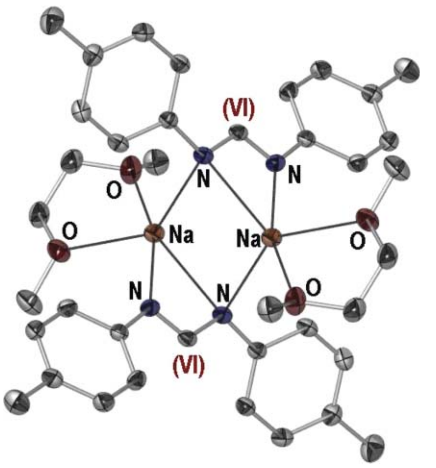

Fig. 17 Molecular structure of [{Na(pTolForm)(DME)}$_2$] (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity.

Preparation and isolation of Na(oMfpForm) in Et$_2$O results in two complexes depending on preparation conditions.[36d] At low temperature a dimer species results, *viz.* [Na$_2$(oMfpFormH)$_2$(Et$_2$O)$_2$], that is distinct from classic type **III**, **VI** or **VII** bridged dimers, *e.g.* [{Li(MesForm)(DME)}$_2$],[40] [{Li(pTolForm)(TMEDA)}$_2$]$_n$[36a] and [{K$_2$(pTolForm)$_2$(THF)$_3$}]$_n$[47] (*vide infra*) respectively. This compound resembles the lithium–THF analogue (Fig. 9) with five- instead of four-coordinate metal centres, *i.e.* type **VI** versus type **III** binding. Five-coordination is effected by chelation by two nitrogen centres of one formamidinate accompanied by nitrogen and *ortho*-F atom donation from the opposing ligand and ether coordination. In stark contrast, preparation at ambient temperature results in partial C–F activation of the low temperature dimer to yield NaF that is incorporated into the low temperature dimer to yield a "*C–F activation stable*" octanuclear product, [{Na$_3$(OMfpForm)$_3$(Et$_2$O)(NaF)}$_2$] (Fig. 18). This remarkable caged species is a homodimer (Fig. 18(a)) that contains two trisodium tris(formamidinate) units (Fig. 18(b)) that, fluorine coordination aside, are comprised of oMfpFormH ligands that coordinate using a **II + III** mode (Fig. 6, *cf.* Fig. 16) to bridge three metal centres with an unusual bridging diethyl ether.[36d] These two fragments encapsulate two equivalents of sodium fluoride *via* twofold chelation of the sodium and five sodium to fluoride interactions (Fig. 18(c)).

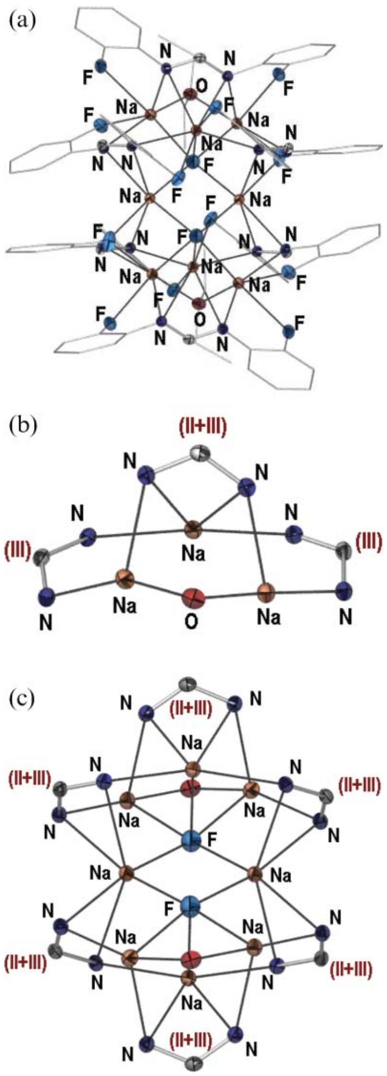

Fig. 18 (a) Molecular structure of [{Na$_3$(oMfpForm)$_3$(μ-Et$_2$O)NaF}$_2$]. Hydrogen atoms omitted for clarity and hydrocarbyl groups depicted as wireframes; (b) Molecular structure of single trisodium tris(formamidinate) diethyl ether capping subunit. Formamidinate binding modes in parentheses. Hydrogen atoms, arylfluoride groups and ether hydrocarbyl groups omitted for clarity; (c) Molecular structure of central cage structure of [{Na$_3$(oMfpForm)$_3$(μ-Et$_2$O)NaF}$_2$]. Formamidinate binding modes in parentheses. Hydrogen atoms, aryfluoride groups and ether hydrocarbyl groups omitted for clarity (POV-RAY illustration, 40% thermal ellipsoids).

Potassium complexes

The bis(aryl)formamidinate chemistry of potassium has the potential to provide the greatest coordination range of all the alkali metals studied by us. The larger potassium ion (1.38 Å; Li 0.76 Å; Na 1.02 Å)[46] presents greater space for ligand coordination and, coupled with the propensity of potassium to interact with aromatic groups,[48] provides for the possibility of new structural motifs. As for the sodium chemistry,

Table 3 Summary of the binding modes, nuclearity and composition of potassium compounds described in this article

Ligand	Solvent	Formula	Nuclearity	Binding mode[a]	Comments	Ref.
pTolForm	THF	$[\{K_2(pTolForm)_2(\mu\text{-}THF)_3\}_n]$	Polymer	**VII**	Three bridging THF donors bridge successive units to give polymer.	47
mTolForm	THF	$[\{K_2(mTolForm)_2(\mu\text{-}THF)_3\}_n]$	Polymer	**VII**	Three bridging THF donors bridge successive units to give polymer.	47
pTolForm	DME	$[\{K_2(pTolForm)_2(\mu\text{-}DME)_3\}_n]$	Polymer	**VII**	Two bridging DME donors bridge successive units to give polymer.	47
DippForm	THF	$[\{K(THF)_2K(DippForm)_2\}_n]$	Polymer	**IX**	$K(DippForm)_2$ units exhibit η^6-arene interactions.	35
DippForm	THF	$[K(DippForm)(THF)_3]$.DippFormH	1	**VIII**	DippFormH H-bonds to $[K(DippForm)(THF)_3]$ using imine acceptor.	35
MesForm	THF	[K(MesForm)(MesFormH)]	1	**VIII**	Both MesForm and MesFormH exhibit η^6-arene interactions. Compound exhibits suppressed reactivity.	34
pTolForm	18-C-6	[K(pTolForm)(18-crown-6)]	1	**II**	Compound exhibits considerable O···H–C H-bonding.	47

[a] See Fig. 2 and 4–6 for illustration of binding modes.

bis(aryl)formamidine precursors can be deprotonated using potassium hydride, however we prefer potassium bis(trimethylsilyl)amide for similar reasons to those provided for sodium bis(trimethylsilyl)amide (*vide supra*). See Table 3 for a full list of potassium compounds described in this article.

Ranging from the least sterically demanding pTolForm complexes to the most sterically demanding ligand system; DippForm in THF, the preparation of $K(formamidinate)_n$ compounds results in polymeric species. Thus, isolation of K(pTolForm) from THF yields $[K_2(pTolForm)_2(\mu\text{-}THF)_3]_n$ (Fig. 19),[47] as does the *meta*-methyl substituted species $[K_2(mTolForm)_2(\mu\text{-}THF)_3]_n$.[47] In these compounds there are two formamidinates bridging and chelating two potassium atoms (**VII**) which lie out of the plane generated by the NCN donor. These $K_2(TolForm)_2$ units are bridged by three THF molecules. When K(pTolForm) is isolated from DME rather than THF, a similar compound is obtained with two DME molecules that chelate and bridge to form a related polymer (**VII**).[47]

Isolation of K(DippForm) from THF results in a polymer containing $[K(DippForm)_2]^-$ units where the potassium ion is sandwiched by two type **VIII** (η^6) formamidinate ligands.[35] These anionic units are linked by $[K(THF)_2]^+$ units that are coordinated by type **IX** coordination. The coordination (**VIII**) mode exemplified by this compound has precedent in prior studies reported by us using MesFormH, wherein attempts to deprotonate MesFormH by $KN(SiMe_3)_2$ in THF consistently gave [K(MesForm)(MesFormH)] (Fig. 20), indicating diminished reactivity of the parent bis(aryl)formamidine.[34] This surprising result was obtained in THF, again demonstrating the affinity of potassium for aryl donation over oxygen donors. Heating of the reaction mixture to 110 °C persistently gave the same species, as did treatment of MesFormH with a ten-fold excess of $[K\{N(SiMe_3)_2\}]$ and introduction of TMEDA to the original reaction medium. It therefore appears that the sandwich complex obtained, with the metal coordinated by two type **VIII** donors (η^6), is a highly thermodynamically stable entity that resists deprotonation. By contrast, treatment of DippFormH with half of an equivalent

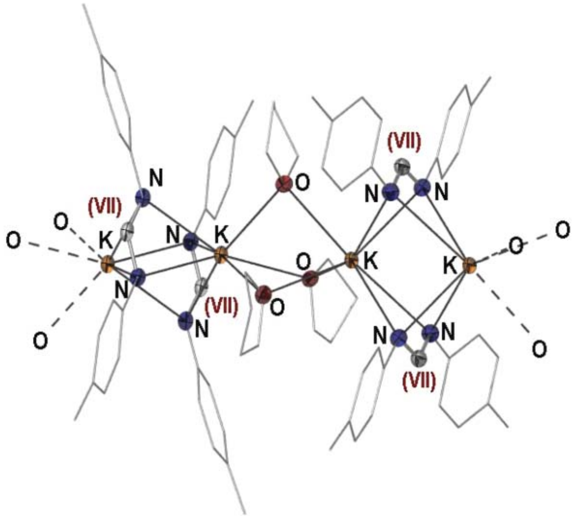

Fig. 19 Molecular structure of repeating unit of $[\{K_2(pTolForm)_2(\mu\text{-}THF)_3\}_n]$ (POV-RAY illustration, 40% thermal ellipsoids). Formamidinate binding modes in parentheses. Hydrogen atoms omitted for clarity and hydrocarbyl groups depicted as wireframes.

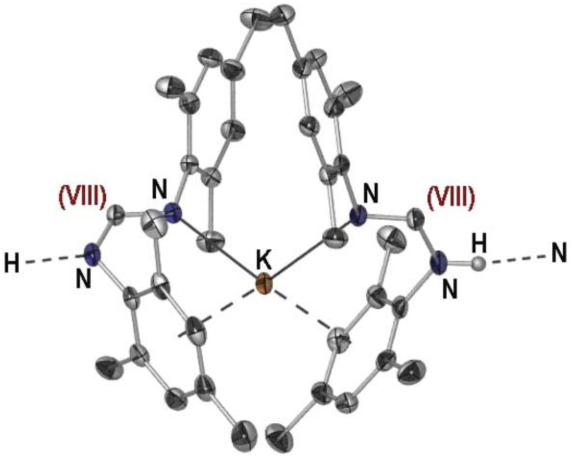

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Fig. 20 Molecular structure of [K(MesForm)(MesFormH)] (POV-RAY illustration, 40% thermal ellipsoids) with hydrogen bonding. Formamidine and formamidinate binding modes in parentheses. All hydrogen atoms, excepting the N–H of MesFormH, omitted for clarity.

of [K{N(SiMe$_3$)$_2$}], in an attempt to prepare a DippForm analogue of [K(MesForm)(MesFormH)], results in the formation of a mononuclear species [K(DippForm)(THF)$_3$]. DippFormH, where the potassium ion is bound by three terminal THF molecules and chelated by a type **VIII** ligand (η^6).[35] The neutral ligand is held by a hydrogen-bond to the imino-*N* atom of the deprotonated ligand. Further studies of the MesForm compound have revealed that only bases with a pK_b of $>$ 40, *e.g.* butylpotassium successfully generate K(MesForm)[49] suggesting that the facile deprotonation of DippForm by weaker bases occurs because of (i) greater arene bulk, which sterically strains the η^6-interaction, and (ii) decreased arene donation resulting from a reduction in the alkyl substituents that assist π-aryl donation.

The only mononuclear compound isolated throughout our studies of potassium was that obtained from the recrystallisation of [K$_2$(pTolForm)$_2$(μ-THF)$_3$]$_n$ in the presence of 18-crown-6.[47] Not surprisingly, the polyether macrocycle binds to the face of the potassium ion, thus inhibiting covalent polymer formation. The solid-state packing of this system is dominated by C–H···O interactions (Fig. 21).

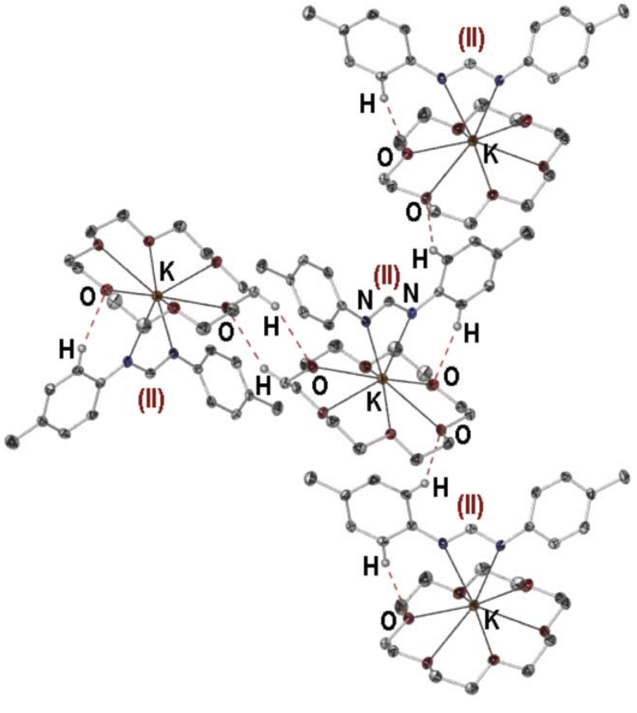

Fig. 21 Extended lattice structure of [K(pTolForm)(18-crown-6)] (POV-RAY illustration, 40% thermal ellipsoids) with hydrogen bonding contacts. Formamidinate binding modes in parentheses. All hydrogen atoms, excepting those involved in hydrogen bonding, omitted for clarity.

Isolation of K(oMfpForm) from THF at ambient temperature did not result in C–F activation unlike the sodium congener (*vide supra*).[36d] Instead, a solvent-free polymer results (*cf.* THF solvated dimers for lithium and sodium) that exhibits extensive fluorine coordination and multiple formamidinate coordination modes. These comprise four potassium atoms that are coordinated by the formamidinate NCN donor set, three *via* type **I** coordination and one by type **II** chelation to give a **III + IV** type ligand (see Fig. 6). This μ_4-amidinate binding mode is unprecedented (Fig. 22(a))[50] and presumably results from fluorine substituents that supplement coordination and frustrate solvation. To this end, one fluorine substituent interacts with the potassium coordinated by a type-**II** amidinate, and the other fluorine interacts with two type-**I** coordinated potassium centres. These interactions are complemented by symmetry generated bis(aryl)formamidinates that create a *stacked* polymer of dimers similar to those generated with the lighter alkali metals (Fig. 22(b)).[36d]

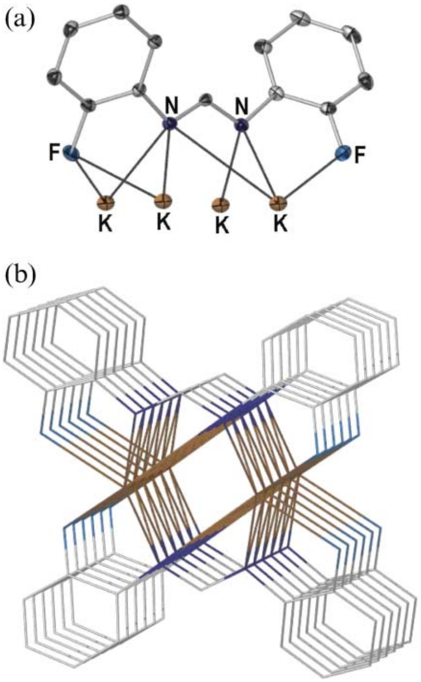

Fig. 22 (a) Molecular structure of one "K(oMfpForm)" unit illustrating μ_4-potassium bridging and **III + VI** binding mode (POV-RAY illustration, 40% thermal ellipsoids). All hydrogen atoms omitted for clarity. (b) Illustration of "K$_2$(oMfpForm)$_2$" unit stacking to generate 1-D polymer.

Concluding remarks

In conclusion, the overview of alkali-metal bis(aryl)formamidinate chemistry provided by this article has underlined the enormous coordinative potential of these ligands and their ability to affect a wide range of synthetic applications.[6–9] It has also highlighted a potential source of diminished reactivity for related ligands when using potassium (*cf.* K(MesForm), Fig. 20).[34] It is conceivable that future explorations of the bis(aryl)formamidinates will uncover much fascinating and useful chemistry. We hope that this article will inspire workers in related fields to apply these ligands to areas of research where their potential remains untapped.

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