Synthesis and characterisation of sodium, potassium, zinc and aluminium formamidinate complexes#

Mehdi Salehisaki,[a] Nazli E. Rad,[a] Peter C. Junk,*[a] Glen B. Deacon,[b] and Jun Wang[a]

[a] College of Science & Engineering, James Cook University Townsville, QLD, 4811, Australia

[b] School of Chemistry, Monash University, Clayton, Victoria, 3800, Australia.

ABSTRACT

The metalation reactions of *N,N'*-bis-(2,4-dimethylphenyl)formamidine (DMFormH) and N,N'-bis-(phenyl)formamidine) (PhFormH) with $KN(SiMe_3)_2$ or $NaN(SiMe_3)_2$ in toluene/ 1,2-dimethoxyethane (dme) resulted in the formation of $[K(DMForm)(dme)]_n$ **(K1)**, $[K_2(PhForm)(N(SiMe_3)_2)]_n$ **(K2)**, $[Na(DMForm)(dme)_2]$ **(Na1)**, and $[Na(PhForm)(dme)]_2$ **(Na2)**. Treatment of PhFormH with $ZnEt_2$ or $AlMe_3$ in toluene/tetrahydrofuran (thf) yielded $[Zn_4(PhForm)_6O].2.5thf$ **(Zn1)**, and $[Al(PhForm)_3]$ **(Al1)** respectively. The potassium-formamidinate compounds (**(K1)** and **(K2)**) are polymeric. **(K1)** has six coordinated potassium with additional C…K interactions. Reducing the steric effect of the formamidinate changes the formamidinate bonding mode. Thus, in the case of the potassium complexes, it led to both inter- and intra-molecular η^6-arene-K binding in **(K2)**. With the sodium complexes, the structure changed from a six-coordinate monomer in $[Na(DMForm)(dme)_2]$ to a five-coordinate dimer in $[Na(PhForm)(dme)]_2$ in which there is an μ_2-1κ(*N,N'*) : 2κ (*N*) formamidinate binding mode. $[Zn_4(PhForm)_6O].2.5thf$ **(Zn1)** has a pseudo-cubane oxide centred cage like structure, whereas $[Al(PhForm)_3]$ **(Al1)** is monomeric with six-coordinate aluminium and chelating formamidinate ligands.

 # We dedicate this paper to Professor Jerry Atwood, a great friend, mentor and colleague, for his outstanding lifetime contributions to chemistry.

Introduction

Amidinate ligands $[R'C(NR)_2]^-$ are attractive because of the variety of bonding modes, the steric shielding of the metal, and the capacity for steric and electronic tuning.[1-5] Although N,N'-diarylformamidines (R' = H) have one less substituent that can be varied, they are attractive because of their facile synthesis from anilines, which can be used to introduce a wide variety of substituents.[6] Alkali metal formamidinates have a history as metathesis reagents [7,8] to prepare complexes of transition metals, main group metals and *f*-block metals.[1-6] In this role lithium formamidinates are potentially more problematic owing to the possibility of lithium halide incorporation in the products, especially in the case of lanthanoid derivatives.[6] In this application, sodium and potassium offer advantages as sodium and potassium halides are less soluble in polar organic solvents, the usual reaction medium. The complexes $[Na_3(p\text{-TolForm})_3(thf)_4]$ (*p*-TolFormH = N,N'-bis(*p*-tolyl)formamidine; thf = tetrahydrofuran) and $[Na_2(p\text{-TolForm})_2(dme)_2]$ were obtained in good yield by treating *p*-TolFormH with sodium hydride or sodium bistrimethylsilylamide, with the latter providing the cleaner reaction.[8,9]

Some potassium analogues were prepared by reaction of potassium hydride with *p*-TolFormH and *N,N'*-bis(m-tolyl)formamidine (*m*-TolFormH).[10] From thf, colorless crystals of $[\{K_2(p\text{-TolForm})_2(thf)_3\}$ and $[\{(K_2(m\text{-TolForm})_2(thf)_3).thf\}_n]$ were obtained. Two other complexes $[\{K(p\text{-TolForm})(dme)\}_n]$ and [K(*p*-TolForm)(18-crown-6)] were synthesized using DME and toluene respectively followed in the latter case by stoichiometric addition of 18-crown-6.[10] [K(*p*-TolForm)(18-crown-6)] was the first example of a poly-ether crown monomeric Group 1 formamidinate complex.

We now report the synthesis and structures of new sodium and potassium formamidinates incorporating the smallest *N,N'*-diarylformamidinate namely *N,N'*-diphenylformamidinate (PhForm) and the bulkier *N,N'*-bis(2,4-dimethylphenyl)formamidinate (DMForm). Reduced bulk can be of interest in formamidinate complexes, as, in the catalysis of the Tishchenko reaction by lanthanum trisformamidinates, the complex of the least bulky example performed best.[11] We have also used the less bulky formamidine PhFormH in reactions with zinc and aluminium alkyls. Previous studies of zinc formamidinates have yielded tetranuclear oxygen centred cages.[12,13] whilst heteroleptic aluminium formamidinates with methyl and chloride coligands are known and have been used in organic synthesis and olefin polymerisation.[14]. Only one homoleptic aluminium formamidinate has previously been

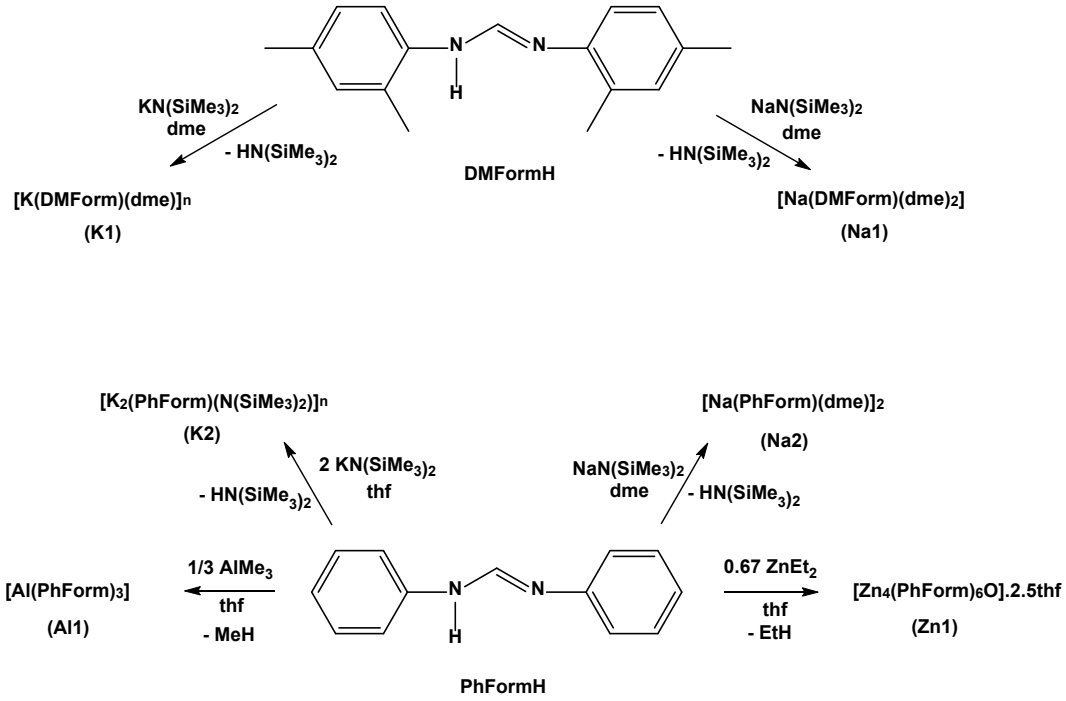
structurally characterized, namely [Al($Me_3SiNCHNSiMe_3$)$_3$].[15], and no homoleptic N,N'-diarylformamidinates.

Results and discussion

1.1. Synthesis and characterization of formamidinate complexes

The potassium and sodium formamidinates, $[K(DMForm)(dme)]_n$ **(K1)** $[K_2(PhForm)(N(SiMe_3)_2)]_n$ **(K2)**, $[Na(DMForm)(dme)_2]$ **(Na1)** and $[Na(PhForm)(dme)]_2$ **(Na2)** were prepared by protolysis reactions of the corresponding alkali metal bistrimethylsiylamides in 1,2-dimethoxyethane by DMFormH or PhFormH (Scheme 1). In the synthesis of **K2**, use of a 2:1 mole ratio of reactants resulted in coordination of a bistrimethylamide ligand rather than dme as in **K1.** The acidity of the hexamethyldisilazane liberated in the reaction (pKa 25.8)[16] is at the low end of the range for amidines (17-30)[17] (in the absence of data for formamidines). $[Zn_4(PhForm)_6O].2.5thf$ **(Zn1)** was obtained by reaction of PhFormH with $ZnEt_2$ in thf while reaction between $AlMe_3$ and PhFormH with stoichiometries of 1:1, 1:2 and 1:3 in thf gave the same product for each, namely $[Al(PhForm)_3]$ **(Al1)** (Scheme 1). The zinc complex has previously been isolated with lattice hexane following preparation of $[ZnCl_2(PhFormH)_2]$ and dehydrohalogenation by methyllithium.[12] The current synthesis (Scheme 1) is much simpler and yields crystals with lattice thf. In these last two preparations, the acidity of the formamidine far exceeds that of the liberated alkane. Overall, yields of crystalline products were in the range 39-85%. Whilst characterization was mainly by X-ray crystallography, the ^{1}H NMR spectra of the complexes were in agreement with the compositions indicated by the X-ray data, except for **Zn1**, where the integration indicated loss of 2 x thf of the lattice solvent. The microanalysis was consistent with this loss. The NC(*H*)N resonances in the ^{1}H NMR spectra (in C_6D_6) at δ = 8.36 (**K1**), 8.78 (**K2**), 8.94 (**Na1**), 8.48 (**Na2**), 8.04 (**Zn1**) and 8.30 (**Al1**) ppm are all at higher frequency than the values for the corresponding formamidines (7.86 and 7.87 ppm) as expected on deprotonation,[12,18,19] and the NH resonance of the formamidines at *ca*. 4.0 ppm was not observed. In addition, the infrared spectra of all complexes were devoid of N-H absorption at ca. 3300 cm^{-1}. Satisfactory microanalyses could only be obtained for **Zn1** and **K2**. Generally values were lower than expected, indicative of decomposition during international travel to the microanalytical service in London, despite crystals being submitted sealed under N_2. Problems with microanalyses of reactive species, e.g. alkaline earth organometallics are well documented in the literature. [20] The source of oxygen in the cage

is probably adventitious water or oxygen [12,13] and the zinc formamidinates seem especially sensitive.



Scheme 1: Synthesis of all formamidinate complexes

1.2. Structural discussion

The polymeric complex $[K(DMForm)(dme)]_n$ **(K1)** (Figure 1) crystallized in the triclinic space group *P*-1, with one monomer moiety in the asymmetric unit. This compound appears to be the first six coordinated potassium formamidinate[21] (but see below). The polymer features μ-1κ (N,N');2κ (N) formamidinate and μ-1κ(O,O'):2κ(O) dme ligands. K1 is linked to one neighbouring potassium by two of the bridging formamidinate ligands, with one chelating and one unidentate bound to K1, and to its other neighbour by two bridging dme ligands, one chelating and the other unidentate bound to K1 (Fig. 1) .This unusual bridging pattern in this polymer has similar dme ligation to that observed in $[K(p\text{-Tolform})(dme)]_n$, but the latter has more symmetrical μ-1κ(N,N'):2κ(N.N') formamidinate bridging and seven coordination.[22] The lower coordination number of **K1** is attributable to the presence of an *ortho*-methyl substituent, which thus has a demonstrable steric effect Compound $[Na_2(p\text{-TolForm})_2(dme)_2]$ has two similar 1κ(N,N'):2κ(N) bridging formamidinate ligands,[23] as do **Na2 and Zn1** below and earlier Zn_4O cages.[12.13] Unsymmetrical bridging dme is very unusual, and has hitherto been observed only in [K(*p*-TolForm)(dme)]n,[22] and the dme complexes of potassium

cyclopentadienide and of a caesium cobalt dicarborane.[21,24] Besides the N and the O donor atoms, four carbon atoms (two Me carbons of dme bridging oxygens, and aromatic ipso and ortho carbons) at 3.2-3.5 Å might be considered as weakly bonding. K-C bond lengths in compounds with terminal η^6-arene-K bonds are in the range 3.1-3.5 Å, [25] thus supporting an interaction from these carbon atoms and raising the coordination number above 6. As C2 and C3 are adjacent to each other, they may interact in an η^2 manner with potassium. However the Me(dme)-K close approach may simply be a consequence of the binding of the bridging oxygens.

Pertinent bond distances and angles are given with Fig 1. Compound **(K1)** has an average K-N bond length (2.85 Å) which is 0.05 Å shorter than in $[K(p\text{-TolForm})(dme)]_n$ [22] The non-bridging oxygen (O2) is closer to K(1) than the bridging oxygen (O1) by 0.11-0.15 Å, but <K-O> (2.83 Å) is very similar to that (2.81 Å) of $[K(p\text{-tolForm})(dme)_2]_n$, consistent with a higher coordination number than six for **K1**. Although the bridgehead C(1) is only 3.159 Å from K(1), a seeming bonding length, the K(1)-C(1)-H(1) angle (152.7°) is not as expected for an η^3-K interaction. The short N-C bond lengths are indicative of delocalisation across the N-C-N backbone of the formamidinate ligand.

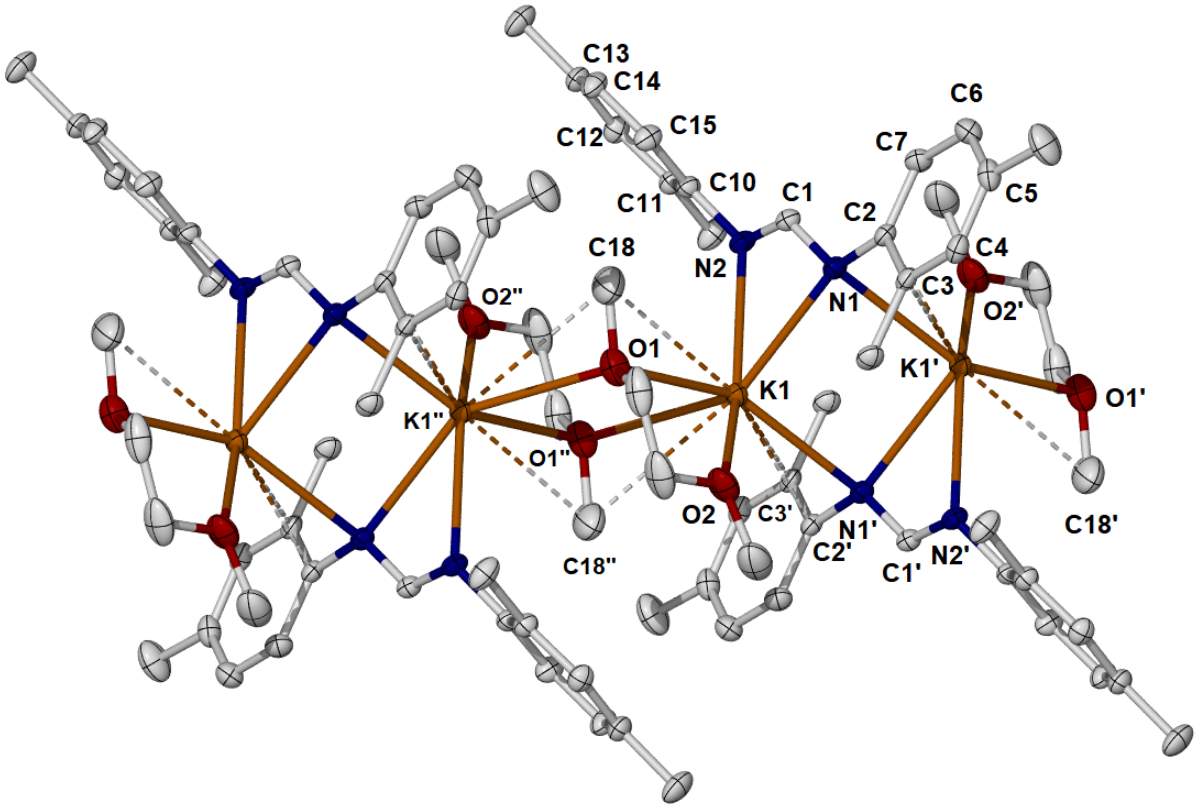
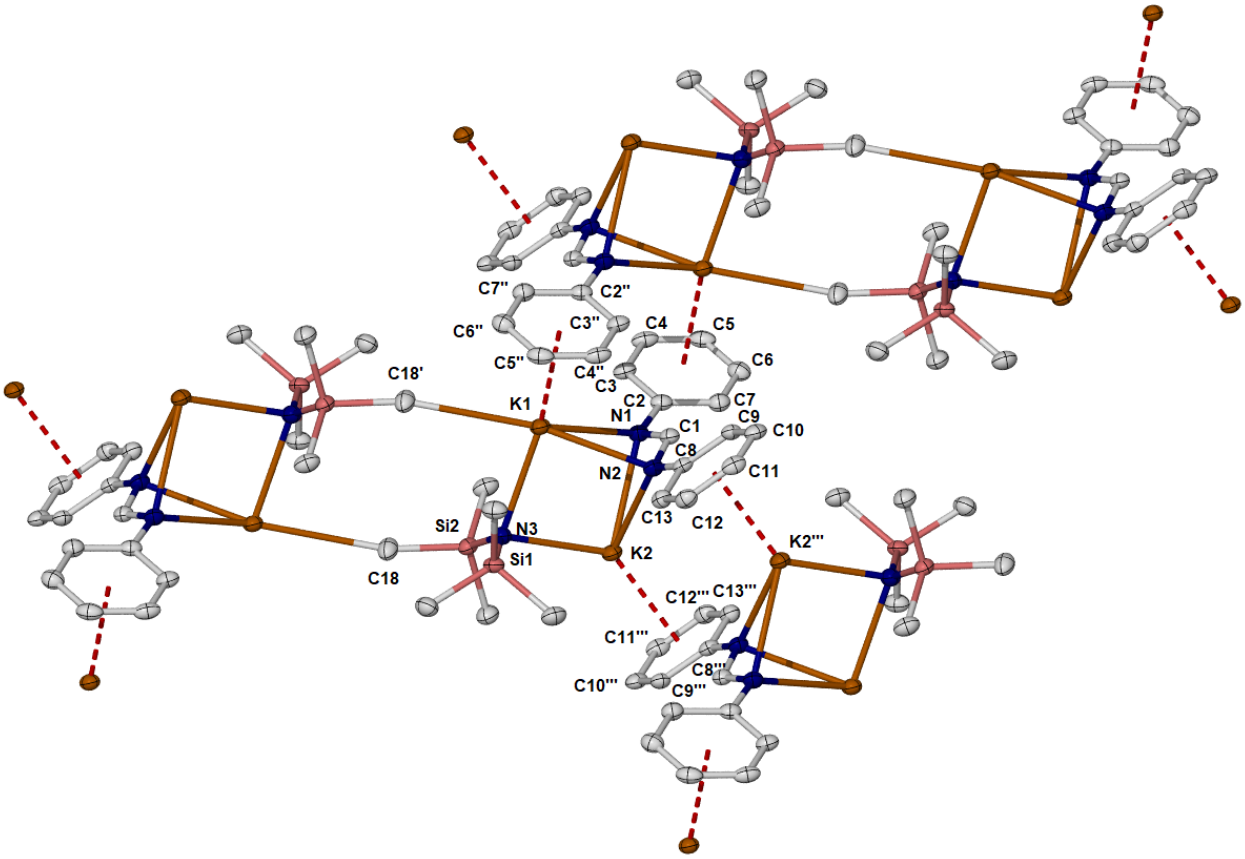


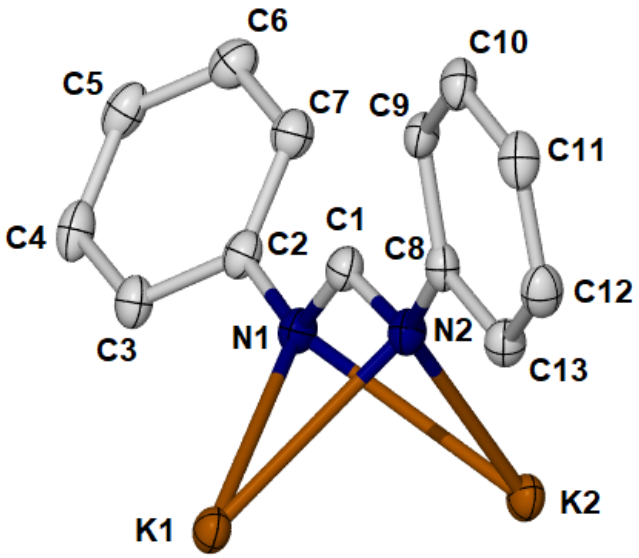
Figure 1. X-ray Molecular structure of $[K(DMForm)(dme)]_n$ **(K1)**. Hydrogen atoms removed for clarity. Selected bond lengths (Å): K(1)-N(1) 2.8229(13), K(1)N(2)2 2.8825(15), K(1)-O(1") 2.9163(14), K(1)-O(1) 2.8930(14), K(1)-O(2) 2.7665(16), K(1)-N(1') 2.9119(15), K(1)-C(2') 3.2284(16), K(1)-C(3') 3.5123(16), K(1)-C(18) 3.444(1), K(1)-C(18") 3.451(2), N(1)-C(1) 1.3279(19), N(1)-C(2) 1.4007(18), N(2)-C(1) 1.3213(18), N(2)-C(10) 1.4052(19), K(1)-C(1) 3.159(1).Symmetry transformation used to generate atoms: ' = 1-z,1-y,1-z; " = -x,1-y,1-z.

$[K_2(PhForm)(N(SiMe_3)_2)]_n$ **(K2) (Figure 2)** crystallized in the triclinic space group *P-1* with one whole $K_2(PhForm)(N(SiMe_3)_2)$ moiety occupying the asymmetric unit. There is one chelating and bridging (K(1) and K(2)) μ-κ(N.N'):2κ(N,N') formamidinate which also forms an intramolecular π- η^6- interaction (K-C 3.373(3)-3.431(3) Å) with K(1) and an intermolecular π-η^6-Ph interaction (K-C 3.201(3)-3.276(2) Å) with a third K atom (K(2')) and one bridging K(1) and K(2)) $-N(SiMe_3)_2$ group. The K-C bond lengths are in the middle of typical π-arene-K interactions (see **K1** above) and the narrow spread of the values in each case also supports the assignment of η^6-bonding in the structure. One methyl from a Me_3Si group forms an agostic interaction with K(1) (K1-C(18) 3.255(3); K(1)-H(18A) 2.88(3); K(1)-H(18B) 2.94(4) Å). The K(1)-C(1)-H(1) (140.0°) and K(2)-C(1)-H(1) (148.5°) angles of the backbone CH are nearer the ideal 90° for η^3 -ligation than in **K1**, thereby suggesting a contribution from this binding to the bridging interaction (Fig, 2(b)). A comparison of the K(1)-C(1) and K(2)–C(1) bond lengths (3.136 and 3.139 Å respectively) with the K(1)-{C(2)-C(7)} (Av. 3.40 Å) and K(2)-{C(8)-C(13)} (Av. 3.250 Å) values in η^6-Ph-K bonding, provides support for binding of the backbone carbon. However this correlation is not unambiguous as the K(1)-C(1) distance in **K1** is similar (3.159 Å) owing to N,N'-K bonding constraints. With the inclusion of all C-K interactions, K(1) is formally seven-coordinate and K(2) six-coordinate.

The formamidinate bridging is similar to that in $[\{K_2(p\text{-TolForm})_2(thf)_3\}_n]$,[22] which otherwise has three bridging thf ligands rather than the inter- and intra-molecular η^6-arene-K bonding and the bridging silylamide of **K2**. Both inter- and intra-molecular η^6-arene-K interactions have been observed in other potassium formamidinates[26,27] though not both in the one structure as in **K2**.

(a)





(b)

Figure 2. (a) X-ray molecular structure of $[K_2(PhForm)(N(SiMe_3)_2)]_n$ **(K2)**. Hydrogen atoms removed for clarity. Selected bond lengths *(Å)* : K(1)-N(1) 2.911(2), K(1)-N(2) 2.879(2), K(1)-N(3) 2.781(2), K(1)-C(2") 3.406(2), K(1)-C(3") 3.431(3), K(1)-C(4") 3.425(3), K(1)-C(5") 3.385(3),

K(1)-C(6") 3.373(3), K(1)-C(7") 3.379(3), K(1)-C(18') 3.255(3), K(1)-H(18A') 2.88(3), K(1)-H(18B') 2.94(4), K(2)-N(1) 2.931(2), K(2)-N(2) 2.783(2), K(2)-N(3) 2.765(2), K(2)-C(8'") 3.249(2), K(2)-C(9'") 3.253(2), K(2)-C(10'") 3.276(2), K(2)-C(11'") 3.272(3), K(2)-C(12'") 3.225(3), K(2)-C(13'") 3.201(3), N(1)-C(1) 1.324(3), N(1)-C(2) 1.410(3), N(2)-C(1) 1.329(3), N(2)-C(8) 1.389(3), K(1)-C(1) 3.136(3), K(2)-C(1) 3.139(3). Symmetry transformation used to generate atoms: **'** = 1-x, 1-y, 2-z; **"** = 1-x, 1-y, 1-z; **'"** = 1-x, -y, 1-z; **(b)** the bridging coordination of the formamidinate between K(1) and K(2) showing the potential η^3-diazaallyl interaction.

[Na(DMForm)(dme)$_2$] **(Na1)** crystallized in the monoclinic space group *C2/c* with the whole monomer occupying the asymmetric unit. Figure 3 shows the X-ray molecular structure of this compound. The coordination number of the metal centre is six and there are two chelating dme molecules and one chelating formamidinate.

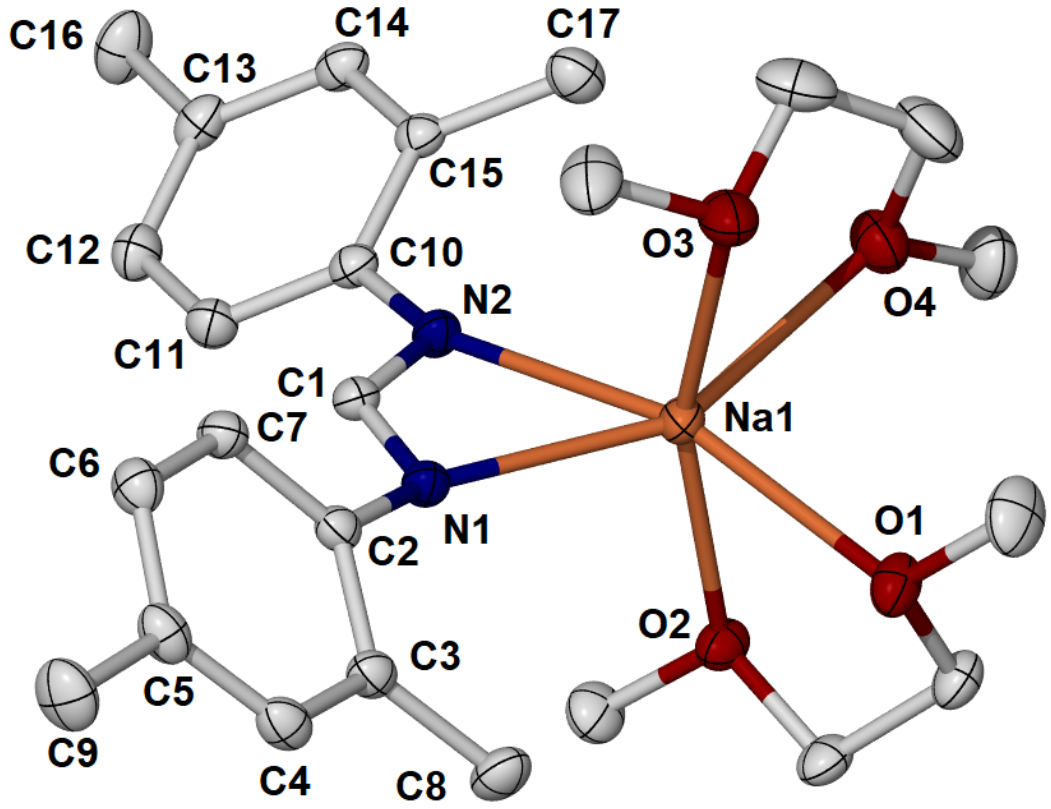


Figure 3. X-ray molecular structure of [Na(DMForm)(dme)$_2$] **(Na1)**. Selected bond lengths (Å): Na(1)-N(1) 2.4102(11), Na(1)-N(2) 2.4840(11), Na(1)-O(1) 2.4928(11), Na(1)-O(2) 2.3686(13),

Na(1)-O(3) 2.4411(15), Na(1)-O(4) 2.4218(11), N(1)-C(1) 1.3265(13), N(1)-C(2) 1.3960(13), N(2)-C(1) 1.3244(13), N(2)-C(1)0 1.4003(14). Hydrogen atoms removed for clarity

Previously, monomeric [Na(XylForm)(dme)$_2$], and [Na(DippForm)(dme)$_2$], have been reported with structures similar to **Na1** [28] The Na-N bond distances for [Na(XylForm)(dme)$_2$], [Na(DippForm)(dme)$_2$], and **Na1** are 2.426(1) Å, 2.411(3) Å and 2.45(ave) Å respectively. These values indicate negligible crowding in these complexes with the bond distances dictated by the Lewis acidity of the metal. A similar conclusion may be drawn from average Na-O bond distances for [Na(XylForm)(dme)$_2$], [Na(DippForm)(dme)$_2$] and **Na1,** namely 2.40 Å, 2.42 Å [28] and 2.43 Å respectively.

[Na(PhForm)(dme)]$_2$ **(Na2)** crystallized in the monoclinic space group *P2$_1$/n* with half the dinuclear centrosymmetric molecule occupying the asymmetric unit (Figure 4). The sodium atom is coordinated by two μ_2 -1κ(*N,N'*) : 2κ(*N*) formamidinate ligands, one chelating and the other unidentate, and one terminal dme. The resulting coordination number is five, and the arrangement of donor atoms around sodium can be described as distorted square pyramidal with a formamidinate nitrogen in the apical position. Although a lower coordination number than in **Na1** appears surprising with a less bulky formamidinate ligand, the reduced crowding enables PhForm, which a better donor than dme, to assume a higher denticity than in **Na1.** Thereafter, reduced Lewis acidity and potential crowding prevents further dme coordination. **Na2** and [Na$_2$(*p*-TolForm)$_2$(dme)$_2$] have similar structures,[23] but so does [Na$_2$(EtForm)$_2$(dme)$_2$] with the bulkier *N,N'*-bis(2,6-diethylphenyl)formamidinate ligand. However, solutions of the last complex in hexane were repeatedly evaporated which would encourage loss of dme. The average Na-N bond length of **Na2** is 2.48 Å which is slightly longer than the corresponding distance in **Na1** (2.44 Å), despite the reduced coordination number, However, the average Na-O bond length (2.38 Å) is less than that of **Na1** (2.43 Å).

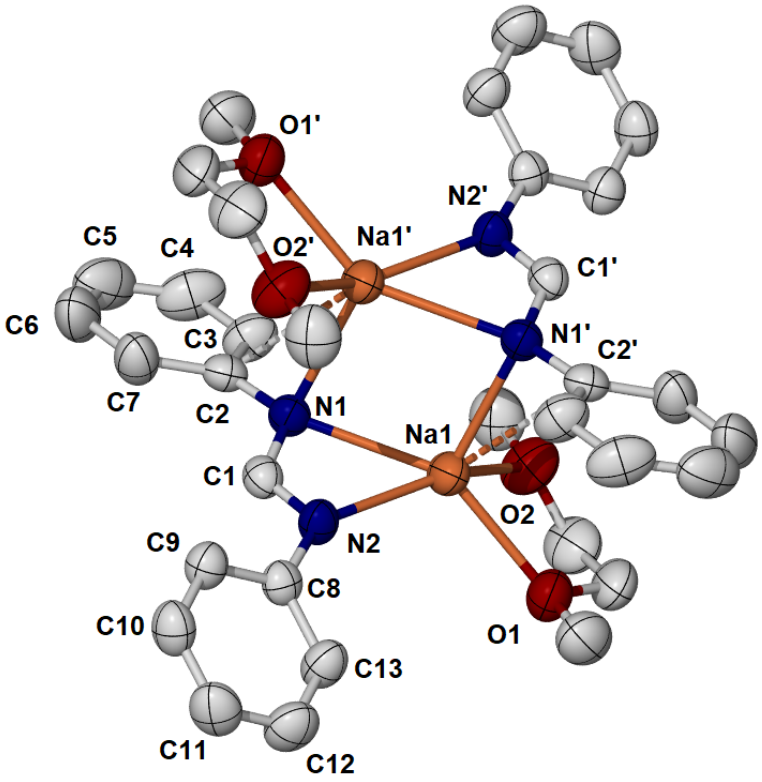


Figure 4. X-ray molecular structure of [Na(PhForm)(dme)]$_2$ **(Na2)**. Selected bond lengths (Å): Na(1)-N(1) 2.576(2), Na(1)-N(2) 2.392(2),Na(1)-N(1') 2.463(2),Na(1)-O(1) 2.380(2),Na(1)-O(2) 2.379(2),Na(1)-C(2') 3.004(3),N(1)-C(1) 1.325(3), N(1)-C(2) 1.401(3), N(2)-C(1) 1.308(3), N(2)-C(8) 1.405(3), Na(1)-Na(1') 3.1931(19).Hydrogen atoms removed for clarity. Symmetry transformation used to generate atoms: ' = 1-x,1-y,1-z.

[Zn$_4$(PhForm)$_6$O].2.5thf **(Zn1)** crystallized in the triclinic space group *P-1* with one whole tetranuclear molecule occupying the asymmetric unit (Figure 5). It contrasts the reported **Zn1**.1.45hexane solvate, which crystallized in the orthorhombic *Pbca* space group.[12] In the cage structure, a central oxygen atom is surrounded by four zinc atoms, which are four coordinate with distorted tetrahedral stereochemistry. There are six mu-1κ(N):2κ(N') ligands, three nitrogen atoms of which bind to each zinc atom, which also binds to the central oxygen. The metrical parameters for Zn-N and Zn-O bonds correspond closely to those reported for the hexane solvate [12], other than marginally less variation, hence they require no further discussion. Presumably the oxygen arises from fortuitous oxygen or water with the stability of the cage making it a good oxygen scavenger. An homoleptic zinc formamidinate has been prepared with the bulkier DippForm ligand, namely [Zn(DippForm)$_2$], but other Zn/DippForm/oxy species were also obtained.[29]

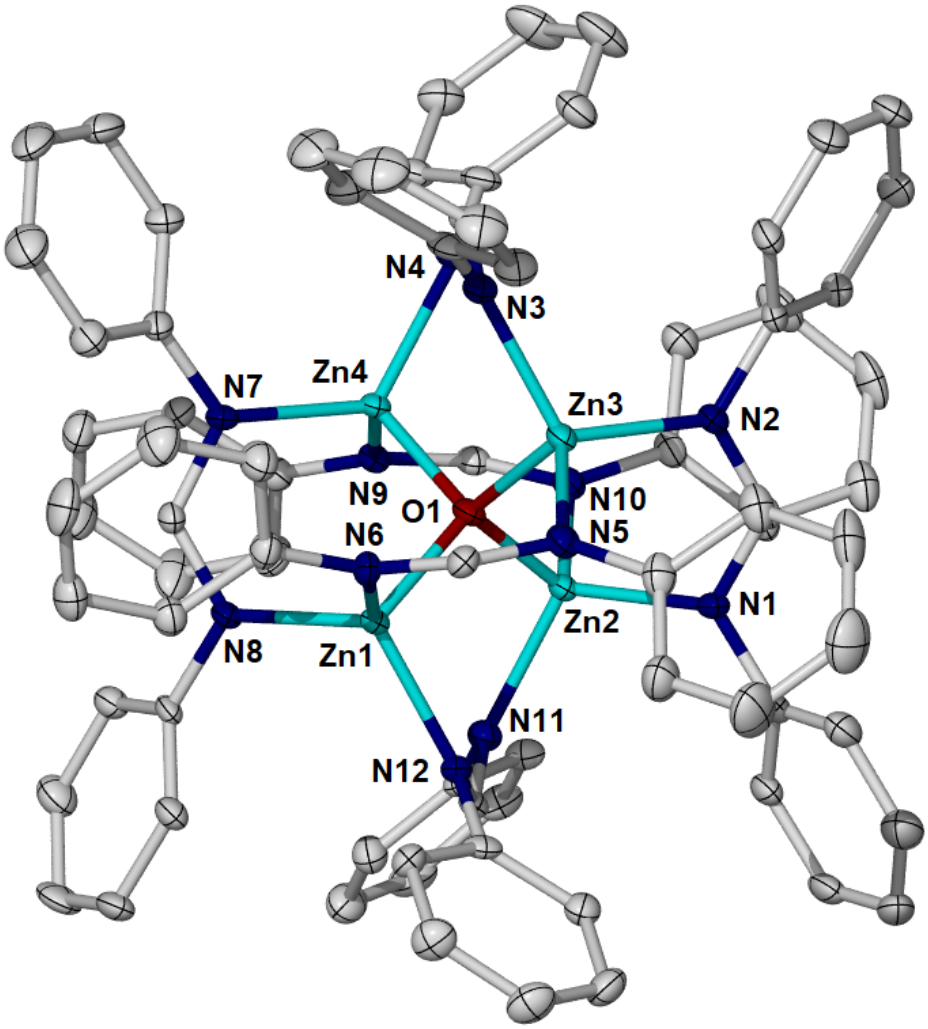


Figure 5. X-ray molecular structure of $[Zn_4(PhForm)_6O].2.5thf$ **(Zn1)**. Selected bond lengths (Å): Zn(1)-O(1) 1.926(3), Zn(1)-N(6) 2.012(4), Zn(1)-N(8) 2.010(4), Zn(1)-N(12) 2.009(4), Zn(2)-O(1) 1.919(3), Zn(2)-N(1) 2.020(4), Zn(2)-N(10) 2.022(4), Zn(2)-N(11) 2.013(4), Zn(3)-O(1) 1.922(3), Zn(3)-N(2) 2.017(4), Zn(3)-N(3) 2.025(4), Zn(3)-N(5) 2.032(4), Zn(4)-O(1) 1.919(3), Zn(4)-N(4) 2.022(4), Zn(4)-N(7) 2.021(4), Zn(4)-N(9) 2.025(4), N(1)-C(1) 1.323(6), N(2)-C(1) 1.327(6), N(3)-C(2) 1.325(6), N(4)-C(2) 1.322(6), N(5)-C(3) 1.325(6), N(6)-C(3) 1.324(6), N(7)-C(4) 1.331(6), N(8)-C(4) 1.319(6), N(9)-C(5) 1.332(6), N(10)-C(5) 1.312(7), N(11)-C(6) 1.322(6), N(12)-C(6) 1.321(6).

$[Al(PhForm)_3]$ **(Al1)** crystallized in the orthorhombic space group *Pccn* and half of the molecule occupies the asymmetric unit (Figure 5). There are three chelating PhForm ligands, two

somewhat unsymmetrical, connected to the metal atom in **Al1** which is thus six

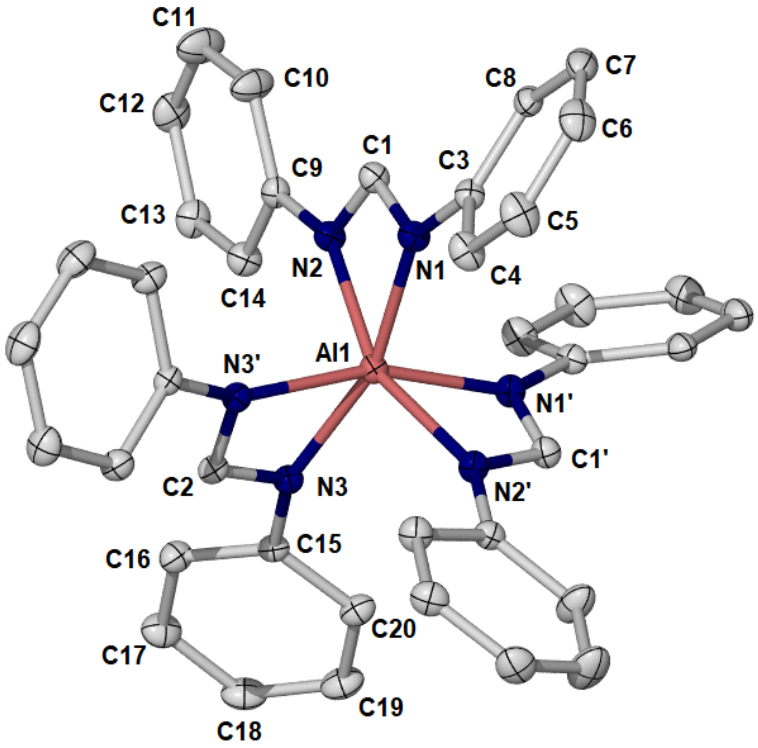


Figure 5. X-ray Molecular structure of [Al(PhForm)$_3$] **(Al1)**. Hydrogen atoms removed for clarity. Selected bond lengths (Å): Al(1)-N(1) 1.9815(18), Al(1)-N(1) 1.9815(18), Al(1)-N(2') 2.0346(18), Al(1)-N(2) 2.0345(18), Al(1)-N(3') 1.9931(18), Al(1)-N(3) 1.9932(18), N(1)-C(1) 1.327(3), N(2)-C(1) 1.324(3), N(3')-C(2) 1.320(2), N(3)-C(2) 1.320(2). Symmetry transformation used to generate atoms: ' = 1/2-X,3/2-Y,+Z.

coordinate. **Al1** is the first homoleptic aluminium *N,N'*-bis(aryl)formamidinate.[29-33] The Al-N bond lengths are similar to those observed in [Al(Me$_3$SiNCNSiMe$_3$)$_3$],[15] which has more symmetrical bonding.

1.3 Conclusions

Two *N,N'*-diarylformamidinates, PhForm and DMForm, with different steric requirements, have been investigated for complexation with sodium and potassium, and to a lesser extent with zinc and aluminium. [K(DMForm)(dme)]$_n$ (**K1**), [K$_2$(PhForm)N(SiMe$_3$)$_2$]$_\infty$ (**K2**), [Na(DMForm)(dme)$_2$] (**Na1**), and [Na(PhForm)(dme)]$_2$ (**Na2**) were prepared by protolysis of potassium or sodium bistrimethylsilylamides with the appropriate formamidine and showed structural variety driven by ligand/metal size variations. In **K2** particularly, 1κ(N,N'):2κ(N,N')

bridging of K(1) and K(2) was skewed towards an η^3 interaction with the metal, and the ligand also bridged a third potassium by an η^6-π-Ph-K interaction, whilst the other Ph group formed an intramolecular η^6 interaction with K(1). These compounds have potential as metathesis reagents. In addition by protolysis of suitable metal alkyls with PhFormH, $[Zn_4(PhForm)_6O].2.5thf$ (**Zn1**) and $[Al(PhForm)_3]$ (**Al1**) were prepared , the latter being the first structurally characterized homoleptic aluminium *N,N'*-diarylformamidinate.

1.4 Experimental

1.4.1 General

All samples were prepared using a glove box, Schlenk flask and vacuum line techniques in an inert atmosphere since the reagents and their products are air-sensitive and moisture sensitive. Sodium or sodium/benzophenone was used for refluxing and distillation of solvents to dry and deoxygenate them prior to use in reactions. PhFormH was purchased from Aldrich and DMFormH was prepared by a literature method.[34] Trimethylaluminium), sodium bis(trimethylsilyl)amide), diethylzinc and potassium bis(trimethylsilyl)amide were purchased from Aldrich and used as received. IR data were obtained from Nujol mulls for the region 4000-400 cm^{-1} with a Nicolet-Nexus FT-IR spectrometer. ^1H NMR spectra were recorded with a Bruker AscendTM 400 (400 MHz) spectrometer using dry degassed perdeuterobenzene as solvent, and resonances were referenced to the residual ^1H resonances of the deuterated solvent. Melting points of the compounds were measured using crystals of compounds in sealed glass capillaries under nitrogen. Elemental analyses (C, H, N) were performed by the Micro analytical Laboratory, Science Centre, London Metropolitan University, England.

$[K(DMForm)(dme)]_n$ (K1)

Potassium bis(trimethylsilyl)amide (10 mL of a 0.5 M solution in toluene; 5 mmol) was added by a syringe to a stirring solution of DMFormH (1.25g; 5 mmol) in dme (20mL) using a Schlenk line. After 1 h stirring, the solution was concentrated to ~10 mL, and colourless crystals of the product formed at room temperature after 1 h. Yield = 1.26 g (59%); M.P. 240-246 ^oC; IR (crystal oil): ν = 1868 (vw), 1768 (vw), 1659 (s), 1606 (m), 1537 (m), 1458 (vs), 1377 (vs), 1298 (vs), 1241 (m), 1203 (vs), 1151 (m), 1120 (m), 1080 (m), 1033 (m), 1008 (s), 996 (m), 936 (m), 887 (m), 849 (w), 815 (s), 771 (m), 720 (m), 610 (m) and 553 (s) cm^{-1}; ^1H NMR (C_6D_6, 303.2 K): δ = 2.17 (s, 6H; *o*-CH_3), 2.25 (s, 6H; *p*-CH_3), 2.98 (s, 6H; dme-CH_3), 3.09 (s, 4H; dme-CH_2), 6.92-6.99 (m, 6H; Ar-H), 8.36 (s, 1H, NC(H)N). Elemental analysis calcd. (%) for $C_{21}H_{29}KN_2O_2$ (*M* =380.56 g/mol): C 66.28, H 7.68, N 7.36; Found: C 53.63, H 7.57, N 7.26.

$[K_2(PhForm)(N(SiMe_3)_2)]_n$ (K2)

Potassium bis(trimethylsilyl)amide (10 mL of a 0.5 M solution in toluene; 5 mmol) was added by a syringe to a stirring solution of PhFormH (0.49 g; 2.5 mmol) in thf (20mL) using a Schlenk line. After 1 h stirring, the solution was concentrated to ~10 mL, and colourless crystals of the

product formed in room temperature after 1 h. Yield = 0.37g (85%); M.P. 233-237 ^{o}C; IR (crystal oil): ν = 1796 (w), 1721 (vw), 1666 (vw), 1590 (s), 1458 (vs), 1378 (vs), 1168 (vs), 1074 (s), 975 (s), 918 (s), 887 (s), 803 (s), 725 (s), 697 (s), 644 (s) and 591 (s) cm^{-1}; ^{1}H NMR (C_6D_6, 303.2 K): δ = 0.16 (s, 18H; CH_3), 6.93–7.32 (br m, 10H; Ar-H), 8.78 (s, 1 H; NC(H)N). Elemental analysis calcd. (%) for $C_{19}H_{29}K_2N_3Si_2$ (*M* =433.83 g/mol): C 52.6, H 6.73, N 9.68; Found: C 52.7, H 6.59, N 9.52.

[Na(DMForm)(dme)$_2$] (Na1)

Sodium bis(trimethylsilyl)amide (5 mL of a 0.6 M solution in toluene; 3 mmol) was added by a syringe to a stirring solution of DMFormH (0.76g; 3 mmol) in dme (20mL). After 1 h stirring, the solution was concentrated to ~10 mL, and cooled overnight causing the formation of colourless crystals of **(Na1)**. Yield = 0.67 g (49%); M.P. 221-223 ^{o}C; IR (crystal oil): ν = 1869 (vw), 1859 (vw), 1740 (vw), 1712 (vw), 1540 (s), 1458 (vs), 1376 (vs), 1320 (s), 1192 (s), 1154 (s), 1081 (vs), 1030 (vs), 940 (m), 893 (m), 860 (vs), 812 (s), 773 (s), 728 (w), 717 (w), 660 (w), 612 (m), 563 (s) and cm^{-1}; ^{1}H NMR (C_6D_6, 303.2 K): δ = 2.30 (s, 6H; *o*-CH_3), 2.40 (s, 6H; *p*-CH_3), 2.97 (s, 12 H, dme-CH_3), 2.98 (s, 8 H, dme-CH_2), 7.00-7.04 (m, 6H; Ar-H), 8.94 (s, 1H, NC(H)N). Elemental analysis calcd. (%) for $C_{25}H_{39}N_2NaO_4$ (M = 223.27 g.mol^{-1}): C 65.91, H 8.85, N 6.15; Found: C 53.13, H 7.27, N 7.56.

[Na(PhForm)(dme)]$_2$ (Na2)

Sodium bis(trimethylsilyl)amide (5 mL of a 0.6 M solution in toluene; 3 mmol) was added by a syringe to a stirring solution of PhFormH (0.588g; 3 mmol) in dme (20mL) . After 1 h stirring, the solution was concentrated to ~10 mL, and cooled overnight causing the formation of colourless crystals. Yield = 0.43 g (46%); M.P. 220-223 ^{o}C; IR (crystal oil): ν = 1847 (vw), 1784 (vw), 1722 (vw), 1675 (vw), 1648 (m), 1586 (s), 1533 (vs), 1455 (vs), 1377 (vs), 1313 (vs), 1205 (s), 1169 (s), 1075 (s), 1023 (s), 985 (s), 922 (m), 892 (m), 839 (m), 802 (s), 762 (s), 722 (s), 693 (s), 618 (w) and 594 (m) cm^{-1}; ^{1}H NMR (C_6D_6, 303.2 K): δ = 1.49 (s, 6 H, dme-CH_3), 1.94 (s, 4 H, dme-CH_2), 6.52–6.88 (br m, 10H; Ar-H), 8.48 (s, 1 H, NC(H)N). Elemental analysis calcd. (%) for $C_{17}H_{21}N_2NaO_2$ (*M* =308.35 g/mol): C 66.21, H 6.86, N 9.08; Found: C 55.21, H 6.38, N 9.91.

[Zn$_4$(PhForm)$_6$O].2.5thf (Zn1)

$ZnEt_2$ (0.72 mL of a 15 W% solution in toluene; 0.8 mmol) was added by a syringe to a stirring solution of PhFormH (0.23 g; 1.2 mmol) in thf (20mL). After 1 h stirring, the solution was concentrated to ~5 mL, and cooled for one week, causing the formation of colourless crystals

of **(Zn1)**. Yield = 0.58 g (48%); M.P. 245-249 ^{o}C; IR (Nujol oil): ν = 1852 (vw), 1789 (vw), 1723 (vw), 1667 (vw), 1596 (m), 1452 (vs), 1377 (vs), 1337 (vs), 1226 (vs), 1174 (s), 1154 (m), 1079 (s), 1024 (m), 998 (m), 974 (vs), 926 (s), 892 (s), 820 (s), 770 (s), 755 (vs), 695 (vs), 642 (s), 617 (w), cm^{-1} (w); ^{1}H NMR (C_6D_6, 303.2 K): δ = 1.42 (m, 2 H, CH_2), 3.57 (m, 2 H, CH_2) (loss of 2 lattice thf), 6.66–6.96 (br m, 60H; Ar-H), 8.04 (s, 6 H, NC(H)N). Elemental analysis calcd. (%) for $C_{80}H_{70}N_{12}O_{1.5}Zn_4$ (*M* = 1485.02 g/mol; loss of 2thf): C 64.70, H 4.75, N 11.32; Found: C 64.45, H 4.76, N 11.30.

[Al(PhForm)$_3$] (Al1)

A solution of $AlMe_3$ (1 mL of a 2.0 M solution in toluene; 2 mmol) was added dropwise to a solution of PhFormH ligand (1.17g, 6 mmol) in 20 mL thf under vigorous stirring and flow of nitrogen gas. The clear solution was stirred for 1 h at ambient temperature. The solution was evaporated to ~10 mL and cooled slowly. Colourless crystals of the product formed after 2 d. Yield = 0.24 g (39%); M.P. 231-235 ^{o}C; IR (Nujol oil): ν = 1540 (m), 1463 (vs), 1377 (s), 1286 (m), 1263 (s), 1099 (m), 1024 (w), 974 (vw), 896 (vw), 803 (vw), 761 (w), 721 (vw) and 697 (w) cm^{-1}; ^{1}H NMR (C_6D_6, 303.2 K): δ = 6.82–7.05 (br m, 30H; Ar-H), 8.30 (s, 3H, NC(H)N). Elemental analysis calcd. (%) for $C_{39}H_{33}AlN_6$ (*M* =612.69 g/mol): C 76.45, H 5.42, N 13.71; Found: C 73.59, H 6.06, N 12.79.

1.4.2 X-ray crystallography

Single crystals suitable for X-ray crystallography of all compounds were obtained by evaporation and concentration of the reaction solutions (~5 ml) followed by very slow cooling over several days.

Single crystals covered with viscous hydrocarbon oil were mounted on glass fibres or loops. Data were obtained at -1730C (100 K) on the MX1: Macromolecular Crystallography beamline at the Australian Synchrotron, Victoria, Australia. Data collection and integration on the MX1: Macromolecular Crystallography beamline was accomplished using Blu-Ice.[35] The structures were solved using SHELXS or SHELXT and refined by full-matrix least squares on all F2 data using SHELX2014 [36] in conjunction with the X-Seed graphical user interface.[37] All hydrogen atoms were placed in calculated positions using the riding model. Data collection and refinement details are collated below.

[K(DMForm)(dme)]$_n$ (K1)

$C_{21}H_{29}KN_2O_2$ (*M* =380.56 g/mol): triclinic, space group P-1 (no. 2), *a* = 8.8050(18) Å, *b* = 11.029(2) Å, *c* = 12.239(2) Å, *α* = 66.50(3)°, *β* = 85.81(3)°, *γ* = 76.15(3)°, *V* = 1057.9(4) Å^3, *Z* = 2, *T* = 173.15 K, μ(MoKα) = 0.267 mm^{-1}, *Dcalc* = 1.195 g/cm^3, 13005 reflections measured (4.766° ≤ 2Θ ≤ 52.732°), 3854 unique (R_{int} = 0.0195, R_{sigma} = 0.0178) which were used in all calculations. The final R_1 was 0.0332 (I > 2σ(I)) and wR_2 was 0.0829 (all data).

[K$_2$(PhForm)(N(SiMe$_3$)$_2$)]$_n$ (K2)

$C_{19}H_{29}K_2N_3Si_2$ (*M* =433.83 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.6830(19) Å, *b* = 10.887(2) Å, *c* = 12.246(2) Å, *α* = 99.72(3)°, *β* = 104.84(3)°, *γ* = 103.36(3)°, *V* = 1177.9(5) Å^3, *Z* = 2, *T* = 293(2) K, μ(MoKα) = 0.512 mm^{-1}, *Dcalc* = 1.223 g/cm^3, 12890 reflections measured (4.828° ≤ 2Θ ≤ 63.918°), 5670 unique (R_{int} = 0.0461, R_{sigma} = 0.0590) which were used in all calculations. The final R_1 was 0.0823 (I > 2σ(I)) and wR_2 was 0.2374 (all data).

[Na(DMForm)(dme)$_2$] (Na1)

$C_{25}H_{39}N_2NaO_4$ (*M* =223.27 g/mol): monoclinic, space group C2/c (no. 15), *a* = 27.319(6) Å, *b* = 13.891(3) Å, *c* = 15.603(3) Å, *β* = 117.11(3)°, *V* = 5271(2) Å^3, *Z* = 8, *T* = 293(2) K, μ(MoKα) = 0.106 mm^{-1}, *Dcalc* = 1.125 g/cm^3, 47438 reflections measured (3.35° ≤ 2Θ ≤ 63.71°), 7429 unique (R_{int} = 0.0293, R_{sigma} = 0.0165) which were used in all calculations. The final R_1 was 0.0489 (I > 2σ(I)) and wR_2 was 0.1374 (all data).

[Na(PhForm)(dme)]$_2$ (Na2)

$C_{17}H_{21}N_2NaO_2$ (*M* =308.35 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 12.1748(8) Å, *b* = 8.0390(5) Å, *c* = 18.0539(11) Å, *β* = 102.960(3)°, *V* = 1721.98(19) Å^3, *Z* = 4, *T* = 296.15 K, μ(MoKα) = 0.100 mm^{-1}, *Dcalc* = 1.189 g/cm^3, 11220 reflections measured (3.684° ≤ 2Θ ≤ 49.99°), 2782 unique (R_{int} = 0.0391, R_{sigma} = 0.0502) which were used in all calculations. The final R_1 was 0.0480 (I > 2σ(I)) and wR_2 was 0.1274 (all data).

[Zn$_4$(PhForm)$_6$O].2.5thf (Zn1)

$C_{88}H_{86}N_{12}O_{3.50}Zn_4$ (*M* =1629.16 g/mol): triclinic, space group P-1 (no. 2), *a* = 14.673(3) Å, *b* = 15.918(3) Å, *c* = 19.353(4) Å, *α* = 91.90(3)°, *β* = 102.06(3)°, *γ* = 101.16(3)°, *V* = 4324.0(16) Å^3, *Z* = 2, *T* = 173.15 K, μ(MoKα) = 1.150 mm^{-1}, *Dcalc* = 1.251 g/cm^3, 46997 reflections measured (2.158° ≤ 2Θ ≤ 50°), 13977 unique (R_{int} = 0.0386, R_{sigma} = 0.0333) which were used in all calculations. The final R_1 was 0.0601 (I > 2σ(I)) and wR_2 was 0.1808 (all data).

[Al(PhForm)$_3$] (Al1)

$C_{39}H_{33}AlN_6$ (*M* =612.69 g/mol): orthorhombic, space group Pccn (no. 56), *a* = 18.333(4) Å, *b* = 10.794(2) Å, *c* = 16.061(3) Å, *V* = 3178.3(11) Å^3, *Z* = 4, *T* = 100.15 K, μ(MoKα) = 0.103 mm^{-1}, *Dcalc* = 1.280 g/cm^3, 28588 reflections measured (5.06° ≤ 2Θ ≤ 63.8°), 4529 unique (R_{int} = 0.0680, R_{sigma} = 0.0371) which were used in all calculations. The final R_1 was 0.0483 (I > 2σ(I)) and wR_2 was 0.1324 (all data).

1.5 Supplementary Material

The crystal structure data has been deposited with the Cambridge Crystallographic Data Centre, with submission numbers for compound **K1** CCDC 2035927, for compound **K2** CCDC 2035928, for compound **Na1** CCDC 2035930, for compound **Na2** CCDC 2035929, for compound **Zn1** CCDC 2035931 and for compound **Al1** CCDC 2035926, and these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data request/cif.

1.6 Acknowledgements

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1.7 Conflicts of interest

The authors declare no conflicts of interest

1.8 References

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GRAPHICAL ABSTRACT

A range of main group formamidinate complexes were synthesized using PhFormH and DMFormH. The first six coordinated potassium bis(aryl)formamidinate formed ($[K(DMForm)(dme)]_n$ **(K1)**) and changing the ligand to PhFormH with less steric effect led to a different bonding mode of η^6 in $[K_2(PhForm)(N(SiMe_3)_2)]_n$ **(K2)** while two structures of $[Na(DMForm)(dme)_2]$ **(Na1)** and $[Na(PhForm)(dme)]_2$ **(Na2)** were isolated using $NaN(SiMe_3)_2$. $[Zn_4(PhForm)_6O].2.5thf$ **(Zn1)** which has an oxide cage and $[Al(PhForm)_3]$ (**Al1**) were isolated by treating the PhFormH with $ZnEt_2$ or $AlMe_3$.