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Synthesis and structural characterisation of some novel lithium and sodium *N*,*N*′-di(*para*-tolyl)formamidinate complexes

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Treatment of *N*,*N*′-di(*para*-tolyl)formamidine (*p*-tolylformH) (**1**) with LiBu^n in THF, DME or hexane/TMEDA leads to deprotonation of the amidine affording $[Li_2(p\text{-tolylform})_2(THF)_3]\cdot 2THF$ (**2**), $[Li(DME)_3][Li_2(p\text{-tolylform})_3]$ (**3**) and $[\{Li_2(p\text{-tolylform})_2(TMEDA)\}_\infty]$ (**4**) respectively. Similar treatment of **1** with NaH or $[Na\{N(SiMe_3)_2\}]$ in THF or DME yields trinuclear $[Na_3(p\text{-tolylform})_3(THF)_4]$ (**5**) and dinuclear $[\{Na(p\text{-tolylform})(DME)\}_2]$ (**6**). All complexes were characterised by spectroscopy (NMR and IR) and X-ray crystallography. These show *p*-tolylform to be a versatile ligand for alkali metals, exhibiting a wide variety of binding modes, *viz.* μ-η^1:η^1 in **2** and **3** (*i.e.* bridging mode), μ-η^2:η^1 in **4** and **6** (*i.e.* bridging and chelating) and μ-η^2:η^2 (*i.e.* bridging and double chelating) and μ_3-η^2:η^1:η^1 (*i.e.* chelating and bridging between three metal centres) in **5**.

Introduction

Interest in lithium organometallic chemistry has gained considerable attention, and those of anionic N-centred species (lithium amides) are no exception[1] because of their fundamental importance as synthetic reagents in inorganic chemistry and as strong Bronsted bases or nucleophiles in organic synthesis.[2–6] The structures of these complexes, both in solution and solid state, are perceived to be of great importance since they can affect the outcome of syntheses or transformations. Unless sterically hindered ligands are employed, association in the solid state is to be expected due to the high polarity of the Li–N bond.[7–13]

In contrast, sodium amides have been less conspicuous in the literature, mainly due to the lack of any advantage gained in using these highly reactive and more difficult to handle reagents in organic synthesis. However, sodium reagents can offer advantages over lithium reagents in lanthanoid halide metathesis reactions where incorporation of LiX (X = halide) can be problematic.[14] Investigation into the chemistry of sodium amides is therefore warranted.

Di(aryl)formamidinate [ArNCHNAr] ligands have been extensively used in transition metal chemistry, particularly in the preparation of dinuclear paddle-wheel complexes $[M_2(formamidinate)_4]^{0,1,2+}$.[15,16] These ligands are perfectly suited to bridging transition metal centres, permitting extensive study of metal–metal bonded species. Furthermore, the resultant complexes display fascinating magnetic properties through communication of the metals.[15,16] Conversely, main group complexes, particularly those of alkali metals, have received much less attention. Although these complexes have been used extensively in the synthesis of transition metal species, their isolation and characterisation has been ignored.

Potentially, formamidinate ligands of the type $[ArNCHNAr]^-$ are elegant systems for the study of Group 1 metal complexes. This is due to N-donors (sigma and dative coordination), delocalisation of charge across the NCN backbone and facile modification of both steric bulk and electronic properties by substitution of the aromatic rings.

With respect to transition metal chemistry, there are a broad range of crystallographically identified amidinate binding modes with various R groups upon the carbon atom of the backbone (formamidinates; R = H). These include (i) η^1-monodentate where a single metal binds with only one of the nitrogen centres with retention of both single and double C–N bonds on the NCN backbone, *e.g.* $[Pt\{2,6\text{-}(CH_2N\{CH_3\}_2)_2C_6H_3\}\{(4\text{-}CH_3C_6H_4)NC(H)N(4\text{-}CH_3C_6H_4)\}]$,[17] (ii) η^1,η^1-symmetrical diazaallyl, where the NCN backbone chelates the metal with symmetrical M–N and C–N bonds, *e.g.* $[\{Pt((C_6H_5)NC(C_6H_5)N(C_6H_5))\}_2]$,[18] (iii) η^1,η^1-unsymmetrical diazaallyl, where there the M–N and C–N bonds are unsymmetrical, *e.g.* $[Ta(CH_3)Cl_2\{(C_6H_{11})NC(CH_3)N(C_6H_{11})\}_2]$,[19] and (iv) as a μ-η^1,η^1-amidinate, where the ligand can bridge two metals as in the paddle-wheel complexes mentioned earlier, *e.g.* homobimetallic $[Mo_2\{(C_6H_5)NC(C_6H_5)N(C_6H_5)\}_4]$[20] or heterobimetallic $[Pt\{2,6\text{-}(CH_2N\{CH_3\}_2)_2C_6H_3\}Hg\{\mu\text{-}\{(4\text{-}CH_3C_6H_4)NC(H)N(Pr^i)\}\}(Br)(Cl)]$.[21] The facile manipulation of the electronic and steric attributes of amidinates has also made them ideal for Group 13[22–24] catalytic study.[25] Within this field, the group of Jordan have greatly advanced the study of aluminium amidinates.[26–28] In response the corresponding amidinate chemistries of Groups 2,[29] 14[30,31] and heavier Group 13 elements[32,33] have also been studied, thereby furthering the applications potential of p-block species. Lamentably, whilst this has advanced knowledge of chemical reactivity, the development of main group amidinate structural chemistry has not been a principal aim. Indeed, with the exception of cationic aluminium species,[28] the p-block and alkaline earth metal species studied display solely η^2-chelate or η^1:η^1-bridging coordination.[34] In contrast, we believe the structural chemistry of alkali metal formamidinates may possess exceptional structural diversity. This may even exceed that of transition metal species as is borne out by the first structurally authenticated Group 1 formamidinate; $[\{Li(N,N'\text{-di}(para\text{-tolylformamidinate})(Et_2O)\}_2]$,[35] wherein the formamidinate ligand chelates and bridges two different lithium centres *via* μ-η^2,η^1-coordination. This mode of binding is entirely unique throughout the entire amidinate structural archive including benzam-, guan-, and acet-amidinates.[34]

Given the emphasis placed upon Group 1 formamidinates for transition metal syntheses (see above), in particular those of Cotton and co-workers,[36–40] the dearth of crystallographic

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study relating to Group 1 formamidinate species is surprising. One rationale put forward is the facility by which alkali metallated species lose donor solvent.[35] To address this the groups of Arnold[41–44] and Snaith,[45–47] amongst others,[48–56] have reported amid- and guanid-inate alkali metal complexes that are either devoid of labile solvent donors or include Lewis bases of recognised strong donation or chelation. Within this catalogue several discoveries have been made. These include the propensity of potassium species to form solvent free dinuclear di-amidinate μ-η^2,η^2-bound units,[42,51,56] and the likelihood of lithium to give species of greater than mono-nuclearity under an appropriate steric environment.[41,48,53,54] Furthermore, alkali metal studies undertaken within our laboratory have identified a new binding mode for *N*,*N*′-di(aryl)amidinates that has no reported d-, s- or p-block analogue.[57,58] This mode exploits the affinity of heavier alkali metals for aryl–π interactions[59–63] leading to coordination of one formamidinate aryl group together with orthodox η^1-amide bonding; [M{(η^x-Ar)NC(H)N(Ar)}]. Moreover, hitherto some monoazallyl bonding modes have not been observed in metal complexed diazallyl systems like that of amidinates. These include η^3-ligation, as exhibited by *N*-aryl diarylketeneiminates,[64] where the N–C–C fragment interacts with a metal centre placed above/below the azaallyl plane either as part of a symmetrical N–C–C π-donor or as a discrete C=N π-donor. A progression towards this mode has recently been reported for acet- and benz-amidinate complexes of ruthenium pentamethylcyclopentadiene,[65,66] whereupon the metal resides out of the NCN plane in order to maximise interaction with the π-system.

To continue our studies of organoamidolithium chemistry, we now extend our focus to lithiated formamidine complexes, in particular those of *N*,*N*′-di(*para*-tolyl)formamidine (*p*-tolylformH). We also expand this approach to some organoamidosodium chemistry. Herein, we report the synthesis and characterisation of three new lithium formamidinate complexes, *viz.*; $[Li_2(p\text{-tolylform})_2(THF)_3]\cdot 2THF$, $[Li(DME)_3][Li_2(p\text{-tolylform})_3]$ and $[\{Li_2(p\text{-tolylform})_2(TMEDA)\}_\infty]$ and two new sodium formamidinate complexes, *viz.*; $[Na_3(p\text{-tolylform})_3(THF)_4]$ and $[Na_2(p\text{-tolylform})_2(DME)_2]$. In each of these compounds novel structural features are revealed which arise from the variation of solvent conditions. We also report a new crystalline morphology for the parent ligand, *N*,*N*′-di(*para*-tolyl)formamidine.

Results and discussion

N,*N*′-Di(*para*-tolyl)formamidine (**1**) (= *p*-tolylformH) was prepared by a slight modification of the published methodologies of Roberts and Murillo in 79% yield.[35,67,68] The spectroscopic data were essentially the same as that reported by Murillo.[35] *p*-TolylformH was recrystallised from hexane affording large colourless blocks. The compound crystallised in a differing morphology (as determined by X-ray crystallography) to that of Murillo[35] where the recrystallisation was performed from hexanes–toluene (the latter polymorph was also determined by Krygowski *et al.*).[69] The present polymorph crystallises in the monoclinic space group $P2_1/c$ (*cf.* $P\bar{1}$ for Murillo).[35] In both structures the molecules exist as hydrogen bonded dimers arising from N–H ⋯ N interactions between adjacent molecules (Fig. 1, POV-RAY illustration, 30% thermal ellipsoids).[99] In the present case there are two unique molecules in the asymmetric unit. The major difference between the two molecules is the "twist" of the planes defined by the two aromatic rings. In molecule A, the torsion angle is 30.7(1)° and in molecule B, the corresponding angle is 36.8(1)°. In the $P\bar{1}$ polymorph,[35] this angle is 67.1° and in *N*,*N*′-di(*para*-tolyl)acetamidine[70] and *N*,*N*′-di(*para*-tolyl)benzamidine[71] the angles are 68.1 and 86.7° respectively. Other bond lengths and angles in the two polymorphs are similar and show a localisation of electron density between N(2) and C(15) (for bond lengths see Table 1).

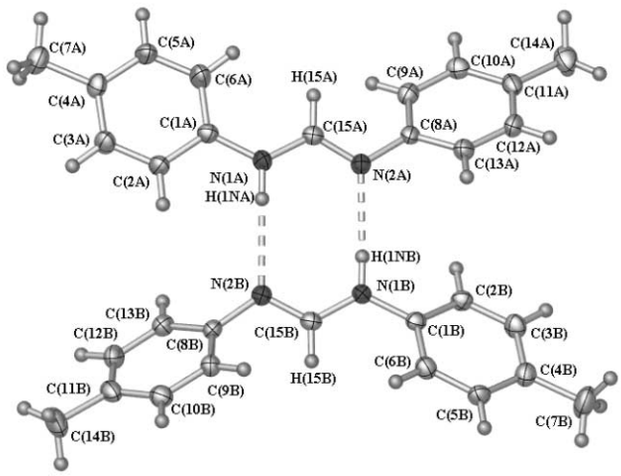
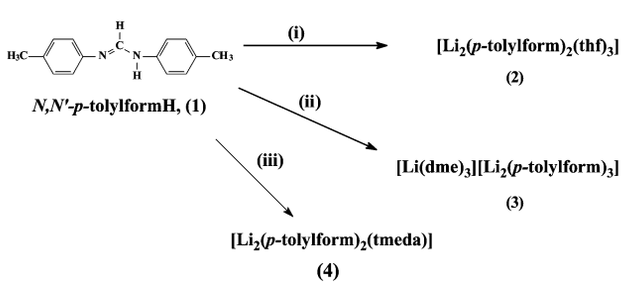


Fig. 1 X-Ray crystal structure of the hydrogen-bonded dimer *N*,*N*′-di(*para*-tolyl)formamidine, (**1**).

Lithium formamidinate complexes

Treatment of *p*-tolylformH with $LiBu^n$ in the coordinating solvents THF (= tetrahydrofuran), DME (= 1,2-dimethoxyethane) or in a non-coordinating solvent in the presence of the potentially chelating amine TMEDA (= *N*,*N*,*N*′,*N*′-tetramethylethylene-1,2-diamine) resulted in clean deprotonation of the amino group yielding $[Li_2(p\text{-tolylform})_2(THF)_3]\cdot 2THF$ (**2**), $[Li(DME)_3][Li_2(p\text{-tolylform})_3]$ (**3**) and $[\{Li_2(p\text{-tolylform})_2(TMEDA)\}_\infty]$ (**4**) respectively (Scheme 1). Spectroscopic



Scheme 1 Reagents and conditions: (i) $LiBu^n$, THF, 0 °C; (ii) $LiBu^n$, DME, rt; (iii) $LiBu^n$, TMEDA, hexane, rt.

evidence confirmed deprotonation. The infrared spectra of **2**–**4** are devoid of any absorptions around 3300 cm^{-1} attributable to N–H stretching frequencies and the ^1H NMR spectra had no resonances at around 12 ppm due to amino protons. The shift in resonances for the proton on the NC(H)N backbone to higher frequency is also indicative of deprotonation. In the free ligand the CH resonance occurs at 7.98 ppm, while in the deprotonated complexes it occurs closer to 9 ppm (8.89 ppm in **2**, 8.88 ppm in **3** and 8.25 ppm in **4**). In all cases, the NMR spectra confirmed the ratio of solvent to *p*-tolylform ligand (obtaining useful NMR spectra was extremely difficult due to solvent loss of the crystalline material, and care was taken to ensure the crystals were not dried *in vacuo* for all analyses). ^{13}C NMR spectra were not very informative due to the relatively insoluble nature of all three lithium complexes in non-coordinating solvents such as C_6D_6 (non-coordinating solvents must be employed in these cases due to potential solvation by the NMR solvent). Attempts to obtain ^7Li NMR spectra for compounds **2**, **3** and **4** were thwarted by solubility problems. There were however weak resonances observable for each compound. For **2**, **3** and **4** there were three, one and two resonances respectively. Taking into account the solid-state structures (see later) there may have been expected one, two and one resonance respectively if the structures are maintained in solution. This indicates that the solution chemistry may be more complex than a singular species and low temperature studies are required.

Table 1 Selected bond distances (Å) and angles (°) for (*p*-tolylformH), **1**

C(1A)–N(1A)	1.411(5)	C(1B)–N(1B)	1.407(5)
C(15A)–N(1A)	1.351(5)	C(15B)–N(1B)	1.342(5)
C(8A)–N(2A)	1.415(5)	C(8B)–N(2B)	1.417(5)
C(15A)–N(2A)	1.293(5)	C(15B)–N(2B)	1.293(5)
N(2A)–C(15A)–N(1A)	121.9(4)	N(2B)–C(15B)–N(1B)	123.1(4)
C(15A)–N(1A)–C(1A)	124.4(4)	C(15B)–N(1B)–C(1B)	123.9(4)
C(2A)–C(1A)–N(1A)	118.4(4)	C(2B)–C(1B)–N(1B)	119.5(4)
C(6A)–C(1A)–N(1A)	124.1(4)	C(6B)–C(1B)–N(1B)	122.6(4)
C(15A)–N(2A)–C(8A)	117.4(3)	C(15B)–N(2B)–C(8B)	115.9(3)
C(9A)–C(8A)–N(2A)	123.6(4)	C(9B)–C(8B)–N(2B)	122.7(4)
C(13A)–C(8A)–N(2A)	119.4(4)	C(13B)–C(8B)–N(2B)	119.7(4)

Table 2 Selected bond distances (Å) and angles (°) for $[Li_2(p\text{-tolylform})_2(THF)_3]\cdot 2THF$, **2**

Li(1)–N(1)#1	2.015(7)	Li(1)–O(2)	2.093(8)
Li(1)–N(2)	2.041(8)	Li(1)–Li(1)#1	2.807(13)
O(1)–Li(1)–N(1)#1	114.0(3)	O(1)–Li(1)–O(2)	102.7(4)
O(2)–Li(1)–N(1)#1	99.7(3)	N(1)#1–Li(1)–N(2)	125.0(4)
O(1)–Li(1)–N(2)	107.5(3)	Li(1)#1–O(2)–Li(1)	84.2(4)
O(2)–Li(1)–N(2)	104.9(3)		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, y, -z+3/2$.

However, at low temperature, the signals are extremely weak due to extreme insolubility. All three lithium complexes lacked thermal stability, decomposing before melting, but compound **4** had higher stability decomposing above 223 °C (*cf.* >132 °C for **2** and >130 °C for **3**).

For complexes **2**, **3** and **4** X-ray quality crystals were isolated, these were extremely air-sensitive and, like $[\{Li(p\text{-tolylform})(Et_2O)\}_2]$,[39] prone to rapid solvent loss. This frustrated the acquisition of meaningful microanalytical data (see Experimental section), however, given the sharpness of decomposition points, the absence of residual impurity peaks in ^{1}H NMR spectra and high yielding syntheses of f-block complexes employing **2**–**4** in metathesis reactions,[58] their microanalytical purity is unquestionable. In order to gain satisfactory XRD data, crystals of **2**–**4** were either rapidly removed from solvent using a highly viscous hydrocarbon oil and mounted on a goniometer immersed in cooled nitrogen gas, or mounted in capillaries under an inert atmosphere with some mother liquor. Selected bond lengths and angles for complexes **2**, **3** and **4** are compiled in Tables 2, 3 and 4 respectively.

Compound **2** crystallises in the monoclinic space group *C*2/*c* with one half of the binuclear complex in the asymmetric unit, the other half being generated by a two-fold rotation axis. The lithium centres are four coordinate in a distorted tetrahedral geometry being bound by two THF ligands and two nitrogen centres of two different *p*-tolylform ligands (Fig. 2, POV-RAY[99] illustrations, 30% thermal ellipsoids; see Table 2 for selected bond lengths and angles). One of the THF ligands is bound terminally, and the other *bridges* the two lithium atoms. The formamidinate ligands act in a bridging mode between the two lithium atoms in a μ-η^1,η^1-fashion (Li(1)–N(1)#1 2.015(7), Li(1)–N(2) 2.041(8) Å). There is no indication of chelation by the potentially chelating NCN fragment (Li(1)–N(1) 3.397(7), Li(1)–N(2′) 2.995(8) Å). This mode of binding for formamidinates is relatively common in the transition metals[15,16] where metal–metal interactions are sought. The $Li–O_{(terminal)}$ distance of 1.996(7) Å is typical for four coordinate Li (*cf.* 1.98(1) Å in $[\{Li(OEt_2)(mtmsap)\}_2]$ (Hmtmsap = 6-methyl-2-trimethylsilylaminopyridine)[72]) and is shorter, as expected, than the $Li(1)–O_{(bridging)}$ distance of 2.093(8) Å (*cf.* 2.059 to 2.193 Å in several other related dinuclear, hexanuclear and polymeric lithium amides[73–75]) for this rare binding mode of THF.

In the only other structurally authenticated formamidinate complex involving lithium, *viz.* $[\{Li(p\text{-tolylform})(Et_2O)\}_2]$,[35] the formamidinate ligands chelate and bridge the lithium centres in a μ-η^2:η^1-fashion, it is remarkable that a simple change of monodentate solvent, from Et_2O to THF, brings about such a dramatic structural change.

Table 3 Selected bond distances (Å) and angles (°) for $[Li(DME)_3][Li_2(p\text{-tolylform})_3]$, **3**

Molecule A			
Li(1)–N(2)	1.973(11)	Li(2)–N(3)	2.012(12)
Li(1)–N(4)	1.996(11)	Li(2)–N(5)	1.982(12)
Li(1)–N(6)	2.027(11)	Li(1)–Li(2)	2.567(15)
Li(2)–N(1)	2.002(11)		
N(2)–Li(1)–N(4)	120.9(5)	O(2)–Li(4)–O(3)	98.4(4)
N(2)–Li(1)–N(6)	119.4(5)	O(2)–Li(4)–O(4)	94.9(5)
N(4)–Li(1)–N(6)	118.4(5)	O(2)–Li(4)–O(5)	166.4(6)
N(1)–Li(2)–N(3)	119.3(6)	O(2)–Li(4)–O(6)	92.2(4)
N(1)–Li(2)–N(5)	119.4(6)	O(3)–Li(4)–O(4)	79.7(4)
N(3)–Li(2)–N(5)	120.0(5)	O(3)–Li(4)–O(5)	91.8(4)
O(1)–Li(4)–O(2)	78.6(4)	O(3)–Li(4)–O(6)	167.5(5)
O(1)–Li(4)–O(3)	90.7(5)	O(4)–Li(4)–O(5)	95.8(4)
O(1)–Li(4)–O(4)	167.5(5)	O(4)–Li(4)–O(6)	93.0(5)
O(1)–Li(4)–O(5)	92.4(5)	O(5)–Li(4)–O(6)	78.8(4)
O(1)–Li(4)–O(6)	97.9(5)		
Molecule B			
Li(3)–N(7)#1	1.962(11)	Li(3)–N(9)	1.995(11)
Li(3)–N(8)	2.023(11)	Li(3)–Li(3)#1	2.60(2)
N(7)–Li(3)–N(9)#1	120.3(5)	O(7)–Li(5)–O(9)	93.4(2)
N(7)–Li(3)–N(8)#1	120.0(5)	O(7)–Li(5)–O(9)#1	167.1(4)
N(8)–Li(3)–N(9)	118.4(5)	O(8)–Li(5)–O(8)#1	166.6(8)
O(7)–Li(5)–O(7)#1	96.1(6)	O(8)–Li(5)–O(9)	98.6(3)
O(7)–Li(5)–O(8)	79.3(3)	O(8)–Li(5)–O(9)#1	91.8(3)
O(7)–Li(5)–O(8)#1	91.7(4)	O(9)–Li(5)–O(9)#1	78.7(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+1/2$.

Table 4 Selected bond distances (Å) and angles (°) for $[\{Li_2(p\text{-tolylform})_2(TMEDA)\}_\infty]$, **4**

Li(1)–N(1)	2.189(6)	Li(1)–N(2)	2.047(6)
Li(1)–N(1)#1	2.037(6)	Li(1)–N(3)	2.064(6)
N(1)#1–Li(1)–N(1)	106.4(2)	N(1)–Li(1)–N(3)	115.2(3)
N(1)#1–Li(1)–N(2)	123.3(3)	N(2)–Li(1)–N(3)	118.2(3)
N(1)#1–Li(1)–N(3)	115.5(3)	Li(1)–N(1)–Li(1)#1	73.6(2)
N(1)–Li(1)–N(2)	65.25(18)		

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z+1$.

In moving from a monodentate THF solvent to potentially chelating DME, it was of interest to determine what structural changes would take place, and whether the three THF molecules would be substituted by one or two DME molecules. The lithiation of *p*-tolylformH in DME (Scheme 1) resulted in the ionic complex $[Li(DME)_3][Li_2(p\text{-tolylform})_3]$ (**3**) (Fig. 3, POV-RAY[99] illustration, 30% thermal ellipsoids; see Table 3 for selected bond lengths and angles). Compound **3** crystallises in the monoclinic space group *C*2/*c* with one and a half

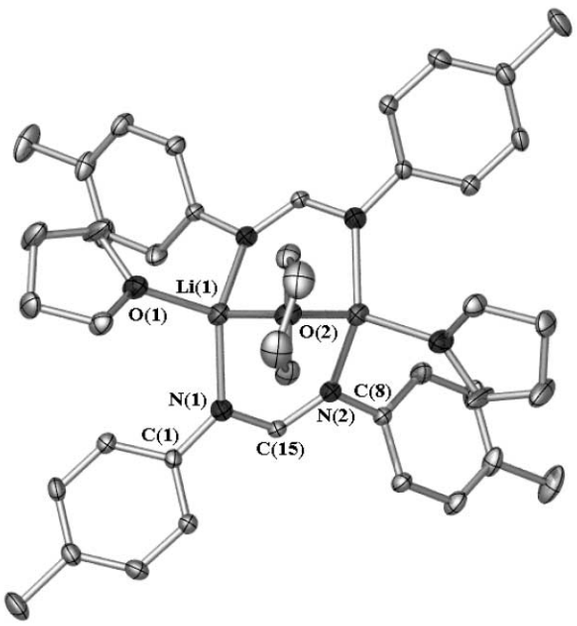


Fig. 2 X-Ray crystal structure of the dinuclear $[Li_2(p\text{-tolylform})_2(THF)_3]\cdot 2THF$, (**2**). The THF molecules of solvation and hydrogen atoms have been omitted for clarity.

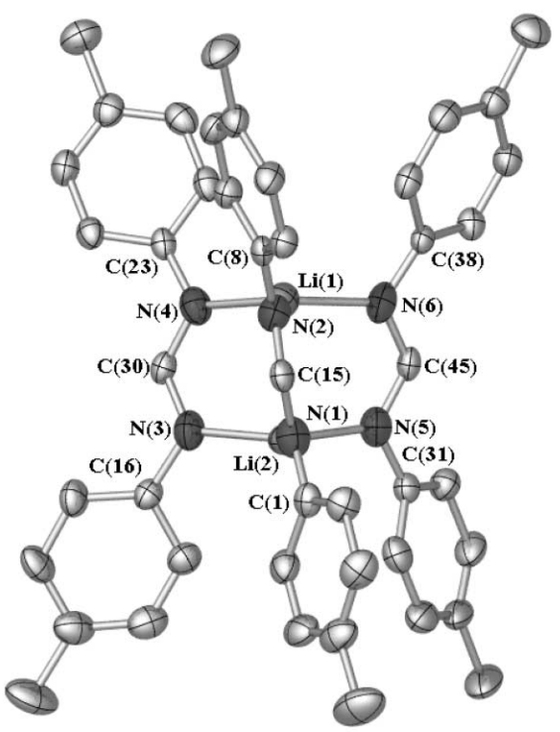


Fig. 3 X-Ray crystal structure of the dinuclear anion in $[Li(DME)_3][Li_2(p\text{-tolylform})_3]$, (**3**). The octahedral cation is unexceptional. Hydrogen atoms have been omitted for clarity.

cation/anion pairs comprising the asymmetric unit. In the anion the *N*,*N*′-di(*para*-tolyl)formamidinate acts a bridging ligand between two lithium centres in a μ-$(form)_3$ binding mode. In the cation a lithium centre is triply solvated by DME, giving a distorted octahedral geometry about the metal centre with the acute O–Li–O angles ranging from 78.6(4)–79.7(4)°. This cation has been previously reported[76,77] and the structural features are unexceptional. The anion, however, is a remarkable binuclear species consisting of two lithium centres and three formamidinate ligands. Each lithium centre has a close to trigonal planar geometry (sum of the three N–Li–N angles for Li(1) = 358.7 and Li(2) = 358.6°) and the formamidinate ligands bridge each of these metal centres with Li–N distances ranging from 1.962(11) to 2.027(11) Å. There appears to be no interaction between the lithium centres and the second nitrogen (Li–N distances range from 3.13(1) to 3.16(1) Å) ruling out any chelation by the ligand. Li(1) and Li(2) sit out of the planes defined by N(2), N(4), N(6) and N(1), N(3), N(5) respectively by 0.13(1) Å.

It is interesting to note that the structural motif of the anion is reminiscent of the paddle-wheel structure that has been found for many transition metals using similar ligand systems.[15,16,78] Considering lithium is smaller than most transition metals it is understandable that only three formamidinate ligands are able to orientate themselves around the two lithium centres, compared with four in the transition metal complexes.

When the lithiation of *N*,*N*′-di(*para*-tolyl)formamidine is carried out in a non-coordinating solvent such as hexane, an insoluble precipitate is generated that is presumably polymeric in nature. When a potentially chelating amine, in this case TMEDA, is added to this mixture, the precipitate dissolves and crystals of $[\{Li_2(p\text{-tolylform})_2(TMEDA)\}_\infty]$ could be isolated. The X-ray crystal structure reveals a polymeric structure where the TMEDA ligand acts as a *bridging* ligand, rather than the more typical *chelate*, between the binuclear lithium complexes. Each lithium centre possesses a distorted tetrahedral geometry (Fig. 4, POV-RAY[99] illustration, 30% thermal ellipsoids; see Table 4 for selected bond lengths and angles). This distortion from 109.5° arises mainly from the small bite angle of the formamidinate ligand (N–Li–N angle 65.25(18)°). Examples of TMEDA acting in a bridging mode rather than chelation are extremely rare in lithium chemistry (a Cambridge crystallographic database search gave only nine hits for organolithium complexes with bridging TMEDA ligands).[79–87] An interesting feature about this particular structure is that, like $[\{Li(p\text{-tolylform})(Et_2O)\}_2]$,[35] not only does the formamidinate ligand act as a bridging ligand but there is a significant interaction with the other nitrogen (Li(1)–N(2), 2.047(6); Li(1)–N(1), 2.189(6) Å) such that the ligand also chelates the metal centre in a μ-η^2:η^1-binding mode. In fact, the structural features of the binuclear unit in compound **4** are very similar to those in $[\{Li(p\text{-tolylform})(Et_2O)\}_2]$[35] where the monodentate Et_2O molecule has been replaced by the bridging TMEDA ligand in **4**. This binuclear core appears to be a recurring feature in Group 1 formamidinate chemistry (see later).

Closer inspection of the lithium to ligand interactions shows there is appreciable contact with the carbon atom of the NCN backbone. Most accepted lithium–carbon bonds range in distance from approximately 2.1–2.37 Å.[88,89] The lithium–carbon distance in the present case is at the upper limits of this range (2.365(6) Å), but indicates a distinct interaction, whereas for $[\{Li(p\text{-tolylform})(Et_2O)\}_2]$[35] it is slightly longer than accepted (2.418 Å) but does not preclude the possibility of very weak carbon lithium interactions. This contact with the carbon atom, coupled with the N–C distances on the backbone (N(1)–C(15) 1.338(8) and N(2)–C(15) 1.303(8) Å) and the asymmetric Li–N distances, suggest the bonding pattern is more akin to a direct Li–N bond and an η^2-interaction with the N=C fragment. This type of bonding is unprecedented in formamidinate chemistry. However, localisation of amidinate electron density has precedent in lithium studies recently reported by the group of Arnold,[44] wherein the use of a bulky terphenyl substituted benzamidinate ligands affords an η^1-amide bound amidinates that exhibit discrete single and double C–N bonds (*e.g.* $[Li\{Pr^iNC(2,6\text{-}(2,4,6\text{-}Pr^i_3C_6H_2)C_6H_3)NPr^i\}(TMEDA)]$; NCN C–N length disparity 0.052 Å, see Table 1 for C–N and C=N lengths of *p*-tolylformH).

Sodium formamidinate complexes

$[Na_3(p\text{-tolylform})_3(THF)_4]$ (**5**) and $[Na_2(p\text{-tolylform})_2(DME)_2]$, (**6**) were synthesised in good yields (*ca.* 50 and 69% respectively) in THF and DME (Scheme 2). $[Na_3(p\text{-tolylform})_3(THF)_4]$, was

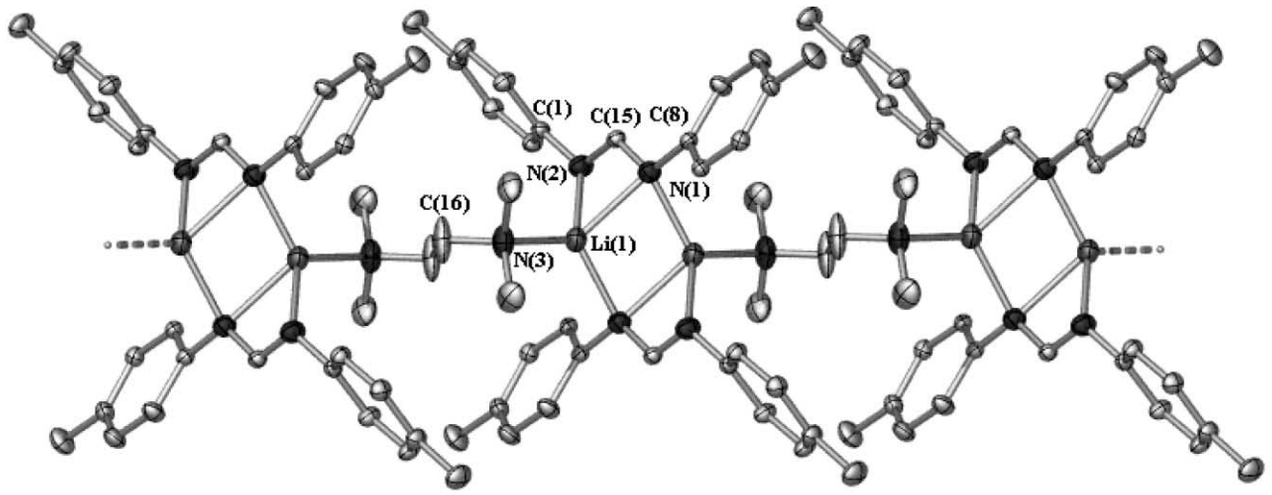
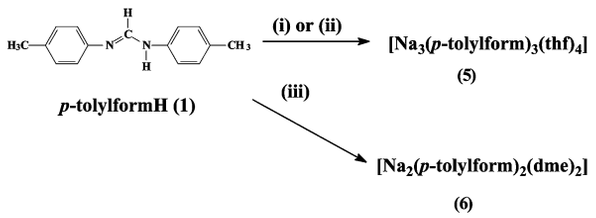


Fig. 4 X-Ray crystal structure of the polymeric structure of $[\{Li_2(p\text{-tolylform})_2(TMEDA)\}_\infty]$, (**4**) showing the unusual bridging mode for TMEDA. Hydrogen atoms have been omitted for clarity.



Scheme 2 Reagents and conditions: (i) $NaN(SiMe_3)_2$, THF, rt; (ii) NaH, THF, rt; (iii) NaH, DME, rt.

synthesised by two methods, *viz*. treatment of *p*-tolylformH with either sodium hydride or by transamination using sodium bis(trimethylsilyl)amide. Since both methods were successful, affording moderate yields of **5**, subsequent reactions were performed using the much cheaper reagent sodium hydride, however, the latter reaction is a cleaner (by ^{1}H NMR, C_6D_6) and simpler synthetic method.

As with the lithium complexes there is a characteristic shift in the ^{1}H NMR spectrum of the NCN backbone hydrogen from 7.98 to 8.80 ppm for compound **5** and to 9.01 ppm for compound **6**. For compound **5** the ratio of the THF to formamidinate ligand was close to 1.3 : 1, in compound **6** the ratio of DME to ligand was 1 : 1, which confirmed the stoichiometry found in the X-ray crystal structures (see below). The ^{13}C NMR spectra were not very informative due to solubility problems resulting in very weak spectra. Both the ^{1}H NMR and infrared spectra, *via* the absence of N–H resonances in the former and N–H stretching frequencies in the latter, confirmed complete deprotonation. Furthermore, the NMR and IR spectra of compound **5** revealed the products obtained by treating *N*,*N*′-di(*para*-tolyl)formamidine with either sodium hydride or sodium bis(trimethylsilyl)amide (Scheme 2) were identical. These complexes, as with the lithium compounds above, were extremely air and moisture sensitive and prone to rapid solvent loss. Care had to be taken in obtaining meaningful NMR data, and furthermore, X-ray structure determinations were very difficult, with many attempts being required to mount suitable crystals bathed in mother liquor. Similarly, as per **2**–**4**, this frustrated the acquisition of microanalytical data for **5** and **6** (see Experimental section). Likewise, in view of their sharp decomposition points and the absence of residual impurity peaks in ^{1}H NMR spectra, we believe them to be of microanalytical purity.

The crystal structure of $[Na_3(p\text{-tolylform})_3(THF)_4]$ (**5**) (Fig. 5, POV-RAY illustration,[99] 30% thermal ellipsoids; see Table 5 for selected bond lengths and angles), reveals a trinuclear species with two structurally distinct sodium environments. In one,

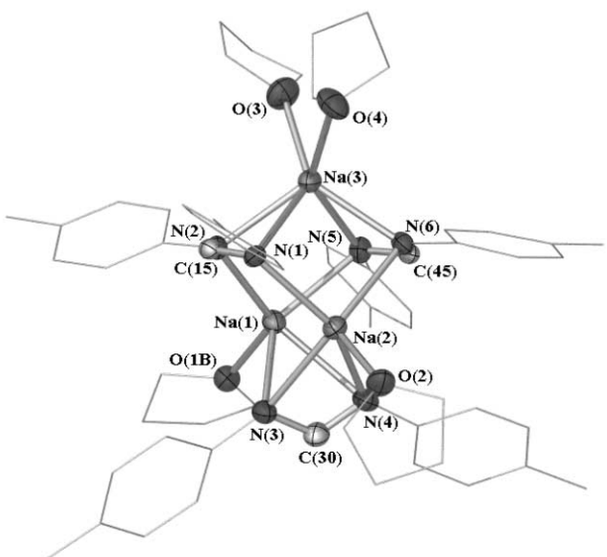


Fig. 5 X-Ray crystal structure of the trinuclear cluster in $[Na_3(p\text{-tolylform})_3(THF)_4]$, (**5**). Tolyl rings and tetrahydrofuran backbones depicted as wire-frames and hydrogen atoms omitted for clarity.

Na(3), the metal is six-coordinate being bound to two terminal THF ligands, and two bidentate formamidinate ligands in a distorted triangular prism,[90] O(3), N(2), N(5) and O(4), N(1), N(6) constituting the triangular faces respectively with the ligand in a μ_3-η^2:η^1:η^1-binding mode (Fig. 5). The other metal centres, Na(1) and Na(2), are five-coordinate being bound by a monodentate THF, a bidentate (chelating) formamidinate and two monodentate (bridging) formamidinate ligands in a distorted square pyramidal geometry.[27] Similarly, the formamidinate ligands have different binding modes. In two ligands (containing N(1), N(2) and N(5), N(6)) the ligands both chelate Na(3), while Na(2) bridges between N(1) and N(6), and N(2) and N(5) bridge Na(1) to Na(3). The remaining formamidinate ligand chelates both Na(2) and Na(1) bridging between the two metal centres in a μ-η^2:η^2-binding mode. The Na–O distances (mean 2.384 Å) are all unexceptional when compared with the mean average structurally characterised Na–O bond (2.450 Å).[91] The Na–N bond distances (2.409(8) to 2.746(10) Å) are slightly longer than established Na–N bond distances in the related $[\{Na(N(SiMe_3)_2)(THF)\}_2]$ (mean 2.397 Å).[92] This is presumably due to the increased coordination number of sodium in the present example. There is one Na ··· N contact of 2.990(8) Å in compound **5** (Na(3)–N(1)), this may be at

Table 5 Selected bond distances (Å) and angles (°) for $[Na_3(p\text{-tolylform})_3(THF)_4]$, **5**

Na(1)–N(2)	2.478(8)	Na(3)–N(1)	2.990(8)
Na(1)–N(3)	2.517(9)	Na(3)–N(2)	2.456(8)
Na(1)–N(4)	2.746(10)	Na(3)–N(5)	2.675(8)
Na(1)–N(5)	2.477(8)	Na(3)–N(6)	2.409(8)
Na(1)–O(1A)	2.45(2)	Na(3)–O(3)	2.389(8)
Na(2)–N(1)	2.467(7)	Na(3)–O(4)	2.361(7)
Na(2)–N(3)	2.645(9)	Na(1)–Na(2)	3.054(4)
Na(2)–N(4)	2.524(9)	Na(1)–Na(3)	3.439(4)
Na(2)–N(6)	2.626(7)	Na(2)–Na(3)	3.476(5)
Na(2)–O(2)	2.335(8)		
O(1A)–Na(1)–N(2)	117.2(7)	O(3)–Na(3)–N(1)	138.5(3)
O(1A)–Na(1)–N(3)	105.6(9)	O(3)–Na(3)–N(2)	105.9(3)
O(1A)–Na(1)–N(4)	114.7(8)	O(3)–Na(3)–N(5)	98.0(3)
O(1A)–Na(1)–N(5)	110.1(8)	O(3)–Na(3)–N(6)	132.4(3)
N(2)–Na(1)–N(3)	95.3(3)	O(4)–Na(3)–N(1)	88.0(3)
N(2)–Na(1)–N(4)	124.3(3)	O(4)–Na(3)–N(2)	125.3(3)
N(2)–Na(1)–N(5)	95.1(3)	O(4)–Na(3)–N(5)	142.7(3)
N(3)–Na(1)–N(4)	51.6(3)	O(4)–Na(3)–N(6)	100.5(3)
N(3)–Na(1)–N(5)	132.7(3)	N(1)–Na(3)–N(2)	49.9(2)
N(4)–Na(1)–N(5)	85.1(3)	N(1)–Na(3)–N(5)	113.3(2)
O(2)–Na(2)–N(1)	109.9(3)	N(1)–Na(3)–N(6)	89.1(2)
O(2)–Na(2)–N(3)	102.9(3)	N(2)–Na(3)–N(5)	90.8(3)
O(2)–Na(2)–N(4)	97.4(3)	N(2)–Na(3)–N(6)	110.2(3)
O(2)–Na(2)–N(6)	117.8(3)	N(5)–Na(3)–N(6)	52.4(2)
N(1)–Na(2)–N(3)	100.9(3)	N(3)–Na(2)–N(6)	126.2(3)
N(1)–Na(2)–N(4)	146.5(3)	N(4)–Na(2)–N(6)	86.8(3)
N(1)–Na(2)–N(6)	96.8(2)	O(3)–Na(3)–O(4)	82.3(3)
N(3)–Na(2)–N(4)	52.7(3)		

Table 6 Selected bond distances (Å) and angles (°) for $[Na_2(p\text{-tolylform})_2(DME)_2]$, **6**

Na(1)–N(1)	2.455(2)	Na(1)–O(1)	2.375(3)
Na(1)–N(2)	2.470(2)	Na(1)–O(2)	2.401(2)
Na(1)–N(2)#1	2.517(3)	Na(1)–Na(1)#1	3.080(2)
O(1)–Na(1)–O(2)	70.50(9)	O(2)–Na(1)–N(2)	135.56(9)
O(1)–Na(1)–N(1)	163.35(9)	O(2)–Na(1)–N(2)#1	118.92(9)
O(1)–Na(1)–N(2)	90.06(10)	N(1)–Na(1)–N(2)	102.28(8)
O(1)–Na(1)–N(2)#1	132.97(10)	N(1)–Na(1)–N(2)#1	55.12(8)
O(2)–Na(1)–N(1)	92.85(9)	N(2)–Na(1)–N(2)#1	103.74(7)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z+1$.

the limits for Na–N binding. Coupled with the Na(3)–C(15) distance of 2.936(11) Å and the asymmetric nature of the NCN backbone (N(1)–C(15) 1.307(9), N(2)–C(15) 1.344(9) Å), this indicates that the binding of formamidinate 'N(1)–C(15)–N(2)' with Na(3) may be more closely defined as η^2:η^1. The $Na–C_{(backbone)}$ (2.888(10) to 3.016(11) Å) distances are slightly longer than established Na–C bond lengths (*e.g.* the mean Na–C bond lengths of 2.76 Å in [{NaCp(DME)}$_\infty$]),[93] indicating there may be some interaction in the present case.

The complex obtained from reaction of sodium hydride with *N*,*N*′-di(*para*-tolyl)formamidine in DME is the dinuclear compound [{Na(*p*-tolylform)(DME)}$_2$] (**6**), with chelating and bridging formamidinate ligands and chelating DME molecules (Fig. 6, Table 6). Thus, each sodium centre sits in a five coordinate distorted trigonal bipyramidal geometry[90] with a chelating formamidinate ligand (from one μ-η^2:η^1-ligand), one monodentate bridging formamidinate (from another μ-η^2:η^1-ligand) and a chelating bidentate DME molecule. The Na–N(bridging) distance of 2.517(3) Å is, as expected, slightly longer than the Na–N (amide) distances in the chelating formamidinate ligand (2.455(2) and 2.470(2) Å). The overall structure of this dinuclear complex is remarkably similar to that of [{Li_2(*p*-tolylform)$_2$(TMEDA)}$_\infty$] (above) and [{Li(di(*p*-tolylform)(Et_2O)}$_2$][35] where the ligands act in bridging and chelating modes and solvent molecules bind at the vacant sites on the metal. In contrast to these similarities, the present work does

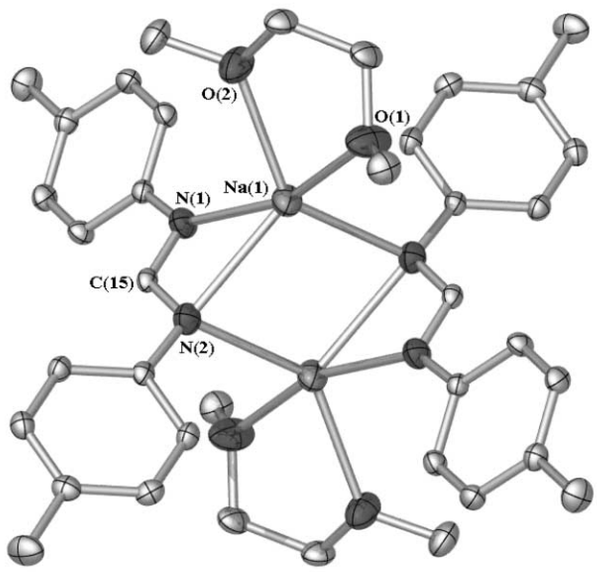


Fig. 6 X-Ray crystal structure of the dinuclear complex $[Na_2(p\text{-tolylform})_2(DME)_2]$, (**6**). Hydrogen atoms have been omitted for clarity.

indeed highlight the remarkable structural changes possible by a simple change in solvent from the monodentate THF in $[Na_3(p\text{-tolylform})_3(THF)_4]$ (**5**) to the bidentate DME in [{Na(*p*-tolylform)(DME)}$_2$] (**6**). The Na–O distances of 2.455(2) to 2.517(3) Å are similar to those of the mean average structurally characterised Na–O bond (2.450 Å).[91] The $Na–C_{(backbone)}$ distances of 2.809(3) Å imply there may be some interaction when compared with known sodium organometallic species, *e.g.* [{NaCp(DME)}$_\infty$] (mean Na–C bond length; 2.76 Å).[93]

In compounds **2** to **6** the NCN backbones (Tables 2 to 6) of the formamidinate ligands are asymmetric with respect to the C–N bonding distances, indicating that the electron density is not totally delocalised even though the ligand is deprotonated (maximum deviation: **2**, 0.01; **3**, 0.035; **4**, 0.024; **5**, 0.042; **6**, 0.022 Å). The degree of localisation, however, is not as pronounced as in the free ligand (Table 1). This type of disparity for deprotonated amidines is rare in main group systems, particularly those of alkali metals (*e.g.* [Li{$(C_6H_5)NC(C_6H_5)N(C_6H_5)$}{$(CH_3)_2NCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)_2$}]; deviation 0.001 Å)[45] but has precedent in η^2-chelate bound *N*,*N*′-symmetrical amidinate complexes of heavy Group 14 metals (*e.g.* [Sn{$(SiMe_3)NC(Bu^t)N(SiMe_3)$}$Cl_2$]; deviation 0.019 Å).[30] This situation is quite different from that observed in closely related carboxylate chemistry where the OCO fragment is typically symmetrical when bound in a bidentate fashion.[94] Intuitively, this suggests that greater aggregation and steric crowding, as in **3** and **5**, induce greater NCN asymmetry.

Conclusions

We have shown that deprotonation of *N*,*N*′-di(*para*-tolyl)-formamidine (*p*-tolylform) with $LiBu^n$, NaH or [Na{$N(SiMe_3)_2$}] in a variety of donor solvents cleanly affords solvated alkali metal complexes. The X-ray crystal structures of these complexes have shown that *p*-tolylform is a versatile ligand for alkali metals, and a wide variety of binding modes are possible. In particular, we have identified *bridging* THF in [Li_2(*p*-tolylform)$_2$($THF)_3$]·2THF, the unusual bridging TMEDA in [{Li_2(*p*-tolylform)$_2$(TMEDA)}$_\infty$], an ionic complex with an unusual [Li_2(*p*-tolylform)$_3$] anion, trinuclear $[Na_3(p\text{-tolylform})_3(THF)_4]$ and dinuclear [{Na(p-tolylform)(DME)}$_2$]. We are currently extending the *p*-tolylform work to heavier Group 1 metals and investigating the s- and f-block structural chemistry of a variety of substituted formamidinates.

Experimental

All reagents were purchased from Aldrich Chemical Company and were used as received. Solvents were purified using standard literature methods[95] and stored in resealable greaseless flasks under an atmosphere of argon. All complexes were highly air and/or moisture sensitive and therefore all manipulations were carried out under an inert atmosphere of argon using standard Schlenk and glove box techniques. The high air and/or moisture sensitivity and extreme ease of solvent loss of compounds **2**–**6** resulted in frustration in obtaining quantitative C, H, and N microanalytical data. Microanalyses for **2**, **3**, **5** and **6** were consistently high in carbon and nitrogen, and low in hydrogen, whilst those of **4** were repeatedly low in nitrogen. ^{1}H NMR spectra were recorded at 300.138 MHz and ^{13}C NMR spectra were recorded at 75.477 MHz using a Bruker BZH 300/52 NMR spectrometer with a Varian console. Chemical shifts were referenced to residual ^{1}H and ^{13}C resonances of the C_6D_6 solvent used. Nuclear magnetic resonance data were also compounded by the rapid loss of incorporated solvent and only after several attempts were spectra with a meaningful ratio of solvent to ligand obtained. IR spectra were recorded as Nujol mulls on NaCl plates using a Nicolet Nexus 670 FTIR spectrophotometer in the range 400–4000 cm^{-1}.

Syntheses

***N*,*N*′-Di(*para*-tolyl)formamidine, 1.** This synthesis followed a slight modification of the published procedure.[67,68] Thus, triethyl orthoformate (11 ml, 0.066 mol) was added to *p*-toluidine (20 g, 0.187 mol) and a few drops of acetic acid and the mixture heated to reflux for 1.5 h. After this time the volatile products were distilled off and the solution was left to cool to room temperature, where a red–orange solid was obtained. This was then recrystallised from boiling absolute ethanol. (Crystals for the X-ray crystal structure were obtained by recrystallization from boiling hexane.) Yield 11.71 g (79%), mp = 140–143 °C. ^{1}H NMR (C_6D_6, δ/ppm) 2.11 (s, 6H, CH_3), 6.88 (d, 4H, aromatics), 6.93 (d, 4H, aromatics), 7.98 (s, 1H, CH). ^{13}C NMR (C_6D_6, δ/ppm) 21.0, 119.6, 130.1, 132.4, 143.8, 150.4. IR (Nujol, NaCl plates) 3304(w), 1942(w), 1878(m), 1747(w), 1668(m), 1588(w), 1574(w), 1310(s), 1202(m), 1172(m), 1112(w), 1038(w), 986(m), 935(m), 808(w), 769(w) cm^{-1}.

[Li$_2$(*p*-tolylform)$_2$THF$_3$]·2THF, 2. *p*-Tolylform (0.73 g, 3.25 mmol) was dissolved in THF. The solution was cooled to 0 °C and LiBu^n (2 ml, 3.2 mmol, 1.6 M in hexanes) was added dropwise providing a clear, yellow solution. The solvent was removed *in vacuo* until an oily residue remained. This was then cooled to −15 °C upon which clear orange crystals were produced, 1.01 g (77%), mp >132 °C (dec.). ^{1}H NMR (C_6D_6, δ/ppm, uncorrected) 1.12 (m, 10H, CH_2), 2.17 (s, 6H, CH_3), 3.29 (m, 10H, CH_2O), 6.93, 7.05, 7.10 (m, 8H, aromatics), 8.89 (s, 1H, CH). ^{13}C NMR (C_6D_6, δ/ppm) 21.0, 25.5, 68.2, 116.5, 121.1, 128.6, 130.0, 130.1. IR (Nujol, NaCl plates) 2360(m), 2342(w), 1670(w), 1603(w), 1548(s), 1500(s), 1325(s), 1219(m), 1203(m), 1180(m), 1111(w), 1045(m), 997(w), 919(w), 891(w), 818(s) cm^{-1}.

[Li(DME)$_3$][Li$_2$(*p*-tolylform)$_3$], 3. *p*-Tolylform (0.86 g, 3.83 mmol) was dissolved in DME and LiBu^n (2.4 ml, 3.84 mmol, 1.6 M) was added dropwise producing a slightly opaque, yellow solution. This solution was left to stand at room temperature and a fine precipitate settled on the bottom of the flask. The solution was filtered, the filtrate reduced *in vacuo* until there was an oily residue left and this was cooled to −15 °C. Upon returning to room temperature orange–brown crystals were formed, 0.86 g (70%), mp >130 °C (dec). ^{1}H NMR (C_6D_6, δ/ppm) 2.18 (s, 6H, CH_3), 2.90 (s, 6H, CH_3, DME), 2.95 (s, 4H, CH_2, DME), 6.90–7.06 (m, 8H, aromatics) 8.88 (s, 1H, CH). ^{13}C NMR (C_6D_6, δ/ppm) 21.0, 59.3, 71.2, 120.4, 129.4, 130.0, 150.9, 162.7. IR (Nujol, NaCl plates) 2360(w), 1886(w), 1664(w), 1568(m), 1549(m), 1500(s), 1338(br m), 1245(w), 1222(m), 1205(m), 1178(w), 1122(m), 1083(s), 1028(w), 995(w), 921(w), 867(m), 831(m), 811(m) cm^{-1}.

[{Li$_2$(*p*-tolylform)$_2$(TMEDA)}$_\infty$], 4. *p*-Tolylform (0.28 g, 1.25 mmol) was partially dissolved in hexane. While stirring, LiBu^n (0.9 ml, 1.44 mmol) was added to the solution and a milky white mixture resulted. The stirring was stopped and the precipitate allowed to settle. To the reaction mixture was added TMEDA (0.2 ml, 1.33 mmol) and with continued stirring, there was a change of colour of the solution from colourless to light orange. The solution was filtered and the solvent reduced to a minimum. This was then left to stand at −15 °C where colourless crystals formed, 0.19 g (53%), mp 223–234 °C (dec.). ^{1}H NMR (C_6D_6, δ/ppm) 1.76 (s, 4H, CH_2N), 1.93 (s, 12H, NCH_3), 2.16 (s, 12H, Ar–CH_3), 6.94, 6.97, 7.01 (m, 16H, aromatics), 8.25 (s, 2H, CH). ^{13}C NMR (C_6D_6, δ/ppm) 21.0, 46.1, 58.4, 119.5, 130.0, 132.3, 148.7. IR (Nujol, NaCl plates) 1670(w), 1545(m), 1501(s), 1309(s), 121(m), 1205(m), 1163(w), 1025(w), 994(w), 931(w), 814(m) cm^{-1}.

[Na$_3$(*p*-tolylform)$_3$(THF)$_4$], 5. *Method I. p*-Tolylform (0.83 g, 3.7 mmol) was dissolved in THF and [Na{N(SiMe$_3$)$_2$}] (3.7 ml, 3.7 mmol) was added slowly to give a yellow–brown solution. The solvent was then reduced until a brown oily residue remained. This was then cooled to −30 °C and orange–brown crystals deposited, 0.60 g (47%), mp >200 °C (dec.). ^{1}H NMR (C_6D_6, δ/ppm) 1.21 (m, 16H, CH_2), 2.22 (s, 18H, CH_3), 3.27 (m, 16H, CH_2O), 6.76–7.01 (m, 24H, aromatics), 8.80 (s, 3H, CH). ^{13}C NMR (C_6D_6, δ/ppm) 21.0, 25.9, 67.9, 116.2, 120.2, 128.9, 130.3, 130.8, 131.3. IR (Nujol, NaCl plates) 1656(s), 1605(w), 1537(s), 1497(s), 1322(s), 1260(w), 1218(m), 1200(w), 1174(m), 1074(m), 1053(w), 997(m), 918(w), 814(s) cm^{-1}.

Method II. p-Tolylform (1.00 g, 4.46 mmol) was dissolved in THF and this was slowly added to a slurry of sodium hydride (0.16 g, 6.67 mmol) in THF. Upon addition, the evolution of hydrogen gas was evident. After gas evolution had ceased, a clear, pale yellow solution with some precipitate remained. The solution was filtered and the solvent reduced to a minimal volume (<1 ml) and placed at −30 °C to yield the title product as colourless crystals, 0.81 g (53%), mp >200 °C (dec.). ^{1}H NMR (C_6D_6, δ/ppm) 1.25 (m, 16H, CH_2), 2.25 (s, 18H, CH_3), 3.44 (m, 16H, CH_2O), 6.75–6.92 (m, 24H, aromatics), 8.76 (s, 3H, CH). IR (Nujol, NaCl plates) 1654(s), 1606(w), 1587(w), 1533(s), 1496(s), 1317(s), 1219(m), 1201(m), 1173(m), 1112(w), 996(m), 930(w), 873(w), 817(s) cm^{-1}.

Synthesis of [Na$_2$(*p*-tolylform)$_2$(DME)$_2$], 6. *p*-Tolylform (0.65 g, 2.89 mmol) was dissolved in DME. This solution was added to an excess of NaH (0.10 g, 4.17 mmol) in DME. Hydrogen gas immediately evolved. After the evolution of gas had ceased a pale yellow solution remained. The solution was filtered to remove any excess NaH and solvent was reduced *in vacuo* to the point of crystallisation. The solution was then left to stand at room temperature for 12 hours yielding clear, pale yellow crystals, 0.67 g (69%), mp 138–143 °C. ^{1}H NMR (C_6D_6, δ/ppm) 2.22 (s, 12H, CH_3), 2.80 (s, 12H, CH_3O), 2.95 (s, 8H, CH_2O), 6.80–7.03 (m, 16H, aromatics), 9.01 (s, 2H, CH). ^{13}C NMR (C_6D_6, δ/ppm) 21.1, 59.0, 71.3, 120.1, 128.9, 130.1, 151.4. IR (Nujol, NaCl plates) 1880(w), 1667(w), 1561(w), 1538(s), 1499(m), 1316(br s), 1219(m), 1202(m), 1175(w), 1111(m), 1070(m), 1022(m), 988(s), 922(w), 858(m), 831(m), 816(s), 713(w), 644(w), 586(w) cm^{-1}.

X-Ray crystallography

All X-ray quality crystals were sealed and mounted in thin walled capillaries, with hemispheres of data collected at room temperature on a Bruker SMART CCD diffractometer using

the omega scan mode with total reflections and unique data listed below. Data sets were corrected for absorption using the program SADABS.[96] Structures were solved using direct methods and refined on F^2 using SHELXL97-2[97] with X-SEED as the graphic interface.[98] All molecular structure figures were generated using POV-RAY.[99] Except for **5** (see below), all non-hydrogen atoms were located and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions (riding model) and were not refined. For compound **1** hydrogen atoms were located on the nitrogen atoms and were refined with isotropic thermal parameters. In compound **2** there was a disordered THF molecule residing in the lattice which proved difficult to model successfully but is not involved in the connectivity of the dinuclear complex **2**. For compound **3** systematic absences indicated that the structure may have been of higher symmetry (space group *R*-3*c*) but all attempts to solve the structure failed. For compound **5**, two THF molecules (containing O3 and O4) had either high thermal motion (O3) or were disordered (O4) and these two molecules were isotropically refined. Details of the X-ray data collection and refinements appear below and selected bond lengths and angles are compiled in Tables 1–6.

[(*p*-Tolylform)H], 1. $C_{15}H_{16}N_2$, $M = 224.30$, monoclinic, $P2_1/c$ (no. 14), $a = 15.895(6)$, $b = 11.133(4)$, $c = 14.462(5)$ Å, $\beta = 95.436(7)°$, $V = 2547.6(16)$ Å^3, $Z = 8$, $D_c = 1.170$ g cm^{-3}, $\mu_{Mo} = 0.07$ mm^{-1}, $F(000) = 960$, crystal dimensions 0.25 × 0.20 × 0.18 mm, reflections collected = 11099, unique reflections = 3665 ($R_{int} = 0.0985$), $R1$ [$I > 2\sigma(I)$] = 0.075, $wR2$ (all data) = 0.246.

[Li$_2$(*p*-tolylform)$_2$(THF)$_3$]·2THF, 2. $C_{50}H_{70}Li_2N_4O_5$, $M = 820.98$, monoclinic, $C2/c$ (no. 15), $a = 25.155(4)$, $b = 12.8620(18)$, $c = 18.673(3)$ Å, $\beta = 126.940(3)°$, $V = 4828.9(12)$ Å^3, $Z = 4$, $D_c = 1.129$ g cm^{-3}, $\mu_{Mo} = 0.07$ mm^{-1}, $F(000) = 1776$, crystal dimensions 0.25 × 0.25 × 0.15 mm, reflections collected = 8688, unique reflections = 3478 ($R_{int} = 0.0968$), $R1$ [$I > 2\sigma(I)$] = 0.088, $wR2$ (all data) = 0.291.

[Li(DME)$_3$][Li$_2$(*p*-tolylform)$_3$], 3. $C_{57}H_{75}Li_3N_6O_6$, $M = 961.05$, monoclinic, $C2/c$ (no. 15), $a = 36.186(4)$, $b = 20.907(2)$, $c = 26.677(3)$ Å, $\beta = 116.898(2)°$, $V = 17999(4)$ Å^3, $Z = 12$, $D_c = 1.064$ g cm^{-3}, $\mu_{Mo} = 0.07$ mm^{-1}, $F(000) = 6192$, crystal dimensions 0.50 × 0.30 × 0.28 mm, reflections collected = 40820, unique reflections = 12940 ($R_{int} = 0.1440$), $R1$ [$I > 2\sigma(I)$] = 0.087, $wR2$ (all data) = 0.315.

[{Li$_2$(*p*-tolylform)$_2$(TMEDA)}$_\infty$], 4. $C_{36}H_{46}Li_2N_6$, $M = 576.66$, triclinic, $P\bar{1}$ (no. 2), $a = 8.472(3)$, $b = 10.446(3)$, $c = 11.821(4)$ Å, $\alpha = 114.830(6)$, $\beta = 90.847(6)$, $\gamma = 108.264(6)°$, $V = 888.5(5)$ Å^3, $Z = 1$, $D_c = 1.078$ g cm^{-3}, $\mu_{Mo} = 0.06$ mm^{-1}, $F(000) = 310$, crystal dimensions 0.40 × 0.35 × 0.30 mm, reflections collected = 4135, unique reflections = 2533 ($R_{int} = 0.0451$), $R1$ [$I > 2\sigma(I)$] = 0.066, $wR2$ (all data) = 0.2100.

[Na$_3$(*p*-tolylform)$_3$(THF)$_4$], 5. $C_{61}H_{77}N_6Na_3O_4$, $M = 1027.29$, triclinic, $P\bar{1}$ (no. 2), $a = 13.189(3)$, $b = 14.601(3)$, $c = 18.462(4)$ Å, $\alpha = 69.586(4)$, $\beta = 88.714(5)$, $\gamma = 68.047(5)°$, $V = 3066.5(12)$ Å^3, $Z = 2$, $D_c = 1.113$ g cm^{-3}, $\mu_{Mo} = 0.09$ mm^{-1}, $F(000) = 1100$, crystal dimensions 0.30 × 0.30 × 0.20 mm, reflections collected = 14022, unique reflections = 8737 ($R_{int} = 0.1143$), $R1$ [$I > 2\sigma(I)$] = 0.073, $wR2$ (all data) = 0.232.

[Na$_2$(*p*-tolylform)$_2$(DME)$_2$], 6. $C_{38}H_{50}N_4Na_2O_4$, $M = 672.80$, triclinic, $P\bar{1}$ (no. 2), $a = 8.1389(16)$, $b = 10.300(2)$, $c = 12.692(3)$ Å, $\alpha = 72.477(4)$, $\beta = 84.631(3)$, $\gamma = 71.255(45)°$, $V = 960.8(3)$ Å^3, $Z = 1$, $D_c = 1.163$ g cm^{-3}, $\mu_{Mo} = 0.09$ mm^{-1}, $F(000) = 360$, crystal dimensions 0.40 × 0.30 × 0.26 mm, reflections collected = 4421, unique reflections = 2723 ($R_{int} = 0.0483$), $R1$ [$I > 2\sigma(I)$] = 0.070, $wR2$(all data) = 0.212.

CCDC reference numbers 184639–184644.

See http://www.rsc.org/suppdata/dt/b2/b204047f/ for crystallographic data in CIF or other electronic format.

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