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Attenuation of reactivity by product solvation: Synthesis and molecular structure of [K{(η^6-Mes)NC(H)N(Mes)}{(η^6-Mes)-NHC(H)N(Mes)], the first formamidinate complex of potassium

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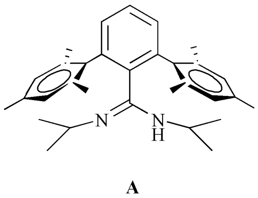
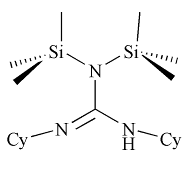
Ambient temperature treatment of the new bulky formamidine (2,4,6-$Me_3C_6H_2$)NC(H)NH(2,4,6-$Me_3C_6H_2$), HFMes, with 0.5 or 1.0 equivalents of potassium hydride or potassium bis(trimethylsilyl)amide yields the first potassium formamidinate complex [K{(η^6-Mes)-NC(H)N(Mes)}{(η^6-Mes)NHC(H)N(Mes)], which displays attenuated reactivity with respect to deprotonation and solvent replacement of the included HFMes ligand.

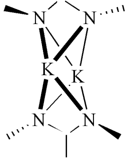
The use of Group 1 amidinate species in the preparation of close-contact bimetallic 'lantern-type' transition metal complexes is a comprehensively studied area of organometallic chemistry.[1,2] In recent times, attention has swayed from traditional d-block based systems to the utility of amidinates as ligands in main group metal based catalysis.[3–5] Given the flexible geometric and steric constraints described by the less encumbered back-bone of formamidinates, it is perhaps surprising that these advances have been made in their absence. Instead, interest has predominantly lain with an ever-growing catalogue of bulky arylamidinates[6–9] and guanidinates,[10] *e.g.* **A** and **B**, that exemplify the versatility of the amidinate frame *via* sterically enforced acute NCN bite angles that suit chelation rather than bridging.



A



B



C

The structural data available for s-block formamidinate compounds is limited to a single report by Cotton and coworkers that describes both [{Li(μ:η^1:η^2-FTolP)(Et_2O)}$_2$] and [(μ-Cl)$_2$(μ-thf){Mg(η^2-FPh)(thf)$_2$}$_2$] (FTolP = di(*para*-tolyl)-formamidinate, FPh = diphenylformamidinate),[11] wherein the facility by which s-block metal formamidinates lose donor-solvent was deemed culpable for the paucity of their structural determination. Our interest in alkali metal formamidinates stems from a desire to prepare unprecedented lanthanoid complexes *via* metathetical paths. In order to frustrate the adverse inclusion of alkali-metal halides in subsequent lanthanoid complexes we have targeted formamidinate complexes of potassium as precursor materials. To date, only three potassium amidinate/guanidinate complexes have been reported.[10,12,13] These unanimously include symmetrical di-potassium di-amidinate subunits, **C**, that exhibit near symmetrical μ:η^2:η^2-diazaallyl bonding with NCN carbon–potassium contacts that approach η^3-diazaallyl ligation (mean NCN plane to NKN plane angle 39.34°).[14] In keeping with the solvent free precedent set by these compounds, herein we describe the preparation of the first structurally characterised potassium formamidinate complex, [K{(η^6-Mes)NC(H)N(Mes)}{(η^6-Mes)NC(H)-NH(Mes)], **1**. Unlike previously reported amidinate/guanidinate complexes of potassium, the molecular structure of **1** is monomeric and incorporates a protonated HFMes ligand that chelates utilising both arene and N-imino functionalities. Furthermore, the diarylformamidinate ligand coordinates in an unconventional near symmetrical NCN η^1-amide mode with unprecedented augmentative η^6-arene group ligation, see Fig. 1. The combination of these interactions affects the attenuated reactivity of the included HFMes moiety.

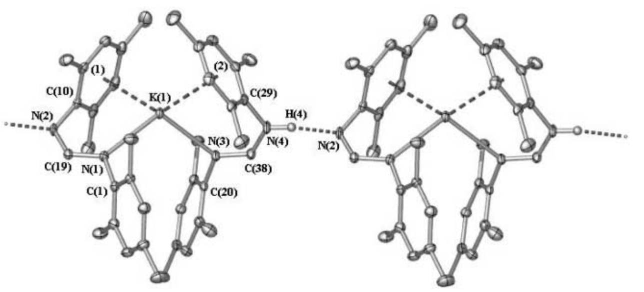


Fig. 1 Hydrogen bonded molecular structure of **1**, except for H(4) all hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): K(1)–N(1) 2.7187(17), K(1)–N(3) 2.7458(16), N(1)–C(19) 1.319(2), N(2)–C(19) 1.324(2), N(3)–C(38) 1.292(2), N(4)–C(38) 1.334(2), K(1)–centroid(1) 2.8867(77), K(1)–centroid(2) 2.8954(75), N(4) ··· N(2)# 2.663(2), H(4) ··· N(2)# 1.80; N(1)–K(1)–N(3) 112.34(5), centroid(1)–K(1)–centroid(2) 122.62(23), N(1)–C(19)–N(2) 126.30(18), N(3)–C(38)–N(4) 124.78(17), C(19)–N(1)–C(1) 117.47(16), C(38)–N(3)–C(20) 116.77(15), N(4)–H(4) ··· N(2)# 166.2.

The sterically encumbered formamidine HFMes was isolated in *ca.* 90% yield utilising an established synthetic protocol.[15] The ambient temperature reaction of tetrahydrofuran or toluene–TMEDA (TMEDA = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine) solutions of HFMes with potassium hydride or potassium bis(trimethylsilyl)amide selectively provides the partially deprotonated compound **1** even when conducted in the

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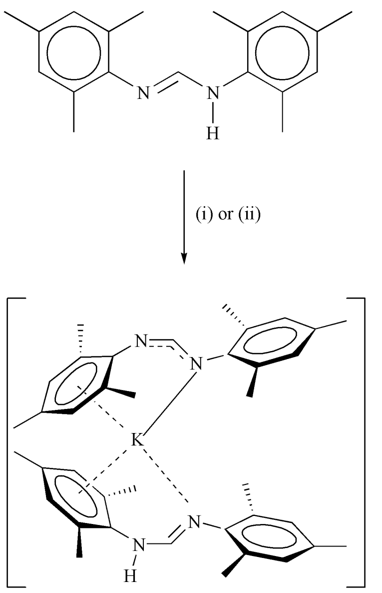

(1)

Scheme 1 Reagents and conditions: (i) 0.5 eq. KH, toluene–TMEDA, ambient temperature, $-H_2$; (ii) 0.5 eq. $[K\{N(SiMe_3)_2\}]$ in toluene, THF, ambient temperature, $-HN(SiMe_3)_2$.

presence of excess potassium reagent, see Scheme 1.‡ Recrystallisation of **1** from fresh tetrahydrofuran can be accomplished in high yield, after washing with cold toluene, giving crystalline samples that incorporate one molecule of toluene in the asymmetric unit.§ Solid samples of $\mathbf{1}\cdot C_6H_5CH_3$ possess high thermal stability (dec. 195 °C) but are sensitive to air and moisture both in solution and the solid-state. Ambient temperature ^1H and ^{13}C NMR spectra of $\mathbf{1}\cdot C_6H_5CH_3$ (d_8-THF) display sharp resonances consistent with a single toluene molecule and broad resonances attributable to the dynamic rearrangement of included formamidine/ate ligands on an NMR time-scale. A low temperature ^1H NMR spectrum of **1** (d_8-THF, −80 °C) exhibits resolved signals for two separate groups of mesityl units, of equal integration, from which the 'bound' and 'unbound' arene-*meta*-proton chemical shifts can be distinguished *via* variable temperature peak coalescence. Both NMR and FTIR data indicate two distinct formamidine/formamidinate ligands by the inclusion of separate $NC(H)N$ resonances (8.22 ppm and 9.13 ppm, HFMes 6.94 ppm) and a singular N–H stretch (3013 cm^{-1}, HFMes 3228 cm^{-1}).

The noteworthy absence of dimer formation in the molecular structure of **1** (Fig. 1) creates a coordination environment about the central metal that does not include close-contact amidinate backbone carbon interactions (K(1)–C(19) 3.632(16) Å), the N(1)–C(19)–N(2) plane : N(1)–K(1)–N(2) plane angle of 5.87(16)° verifying that the FMes ligand of **1** binds without interaction of the NCN π-system. Instead, the coordination sphere of the central metal is saturated by mesityl group π-interactions that more-or-less geometrically oppose the potassium amide/imine interactions. This causes significant distortion of both NCN backbones, rendering C–N bond lengths of 1.319(2)/1.324(2) Å (FMes) and 1.292(2)/1.334(2) Å (HFMes), and NCN angles of 126.30(18)° and 124.78(17)°. The former is obtuse when compared to the mean NCN angle of the η^2-FPh ligands in $[(\mu\text{-}Cl)_2(\mu\text{-thf})\{Mg(\eta^2\text{-FPh})(thf)_2\}_2]$ (117.2°)[11] presumably as a consequence of the enhanced strain imposed by arene–metal interaction. The central potassium geometry generated by the imine, amide and mesityl-centroid donors of **1** is best described as a distended tetrahedron (N(1)–K(1)–N(3) 112.34(5)°, centroid(1)–K(1)–centroid(2) 122.62(23)°, centroid(2)–K(1)–N(3) 83.29(18)°) from which the NCN FMes/HFMes backbone planes and K(1)–N–centroid metallocycles exist at inordinately large torsion angles to one another; 72.90(89)° and 78.32(21)° (resp.). The substantial deformation of the 'formamidinate' frames can be seen in the relative angle of the chelated and non-chelated aryl rings to the N–N vector of their respective formamidine based backbones; HFMes 93.59(81)°, 144.85(71)° and FMes 91.88(78)°, 144.25(85)° respectively. However, the *Z* conformation of both ligands regarding the quasi-imine/amine C–N bonds (FMes and HFMes ligands resp.) has precedent bearing a close resemblance to the FTolP coordination mode described within $[Pd(\eta^5\text{-}C_5H_5)\{(5\text{-Me-2-N(H)CN(4-MeC}_6H_4))C_6H_3\}]$[16] and the η^1-arene interaction of the guanidide lithium complex $[Cd\{N(SiMe_3)_2\}_2Li_2\{PhNC(NPh)NPh\}(thf)_3]$.[17] Irrespective, the η^6:η^1-chelate mode presented by the HFMes/FMes ligands of **1** is entirely unique. Supramolecularly, this facilitates a one-dimensional hydrogen-bonded polymer for **1** resulting from association of the amine proton of the HFMes ligand with a quasi-imine nitrogen of an adjacent unit, see Fig. 1; H(4) ··· N(2)# length of 1.80 Å (sum of hydrogen and nitrogen van der Waals radii 2.500 Å).[18]

The stability of compound **1** is remarkable given its synthesis and characterisation (d_8-THF, NMR) in the presence of coordinating donor solvents. Preliminary results from parallel work conducted within our laboratory suggest that ethereal reactions employing diarylformamidines of lesser steric bulk, *e.g.* HFTolP, render fully solvated complexes, *i.e.* $[\{K(FTolP)(thf)_3\}_\infty]$, even when conducted with excess ligand.[19] The preclusion of TMEDA or THF generated solvated species in the synthesis of **1** ascribes to the retention of the molecular structure in solution. Accordingly, the resilience of **1** to both deprotonation and solvent substitution must result from the inclusion of methyl groups in the arene-2,4,6-positions. These intuitively enhance the electron donation capacity of the aromatic rings *vis-a-vis* the tolyl groups of FTolP. Coordination of protonated amines and ketimines has precedent in lighter Group 1 metallation chemistry, however, in these instances the metallating reagent was either believed to be stoichiometrically deficient,[20,21] or the solvent employed was a weak donor, thereby decreasing the likelihood of NH-ligand displacement and suppressing metallation.[22] Alkali metal arene interactions have been cited as significant stabilising influences in numerous organometallic systems that support unusual coordination environments.[23–26] We believe the molecular structure of **1** epitomises these stabilising influences. Likewise, the stability of **1** with regard to reaction with additional equivalents of potassium hydride or bis(trimethylsilyl)amide can be further rationalised by steric protection afforded by the 2,4,6-methyl substituents. Lastly, the potassium–nitrogen and –η^6-arene centroid bond lengths of 2.7187(17) Å, 2.8867(77) Å and 2.7458(16) Å and 2.8954(75) Å (FMes and HFMes resp.) are considerably abated relative to those deposited in the Cambridge structural database (mean 2.939 Å and 3.116 Å).[14] Work continues in our laboratory upon the preparation and synthetic utility of s- and f-block formamidinate species

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Notes and references

‡ Synthesis of $\mathbf{1}\cdot C_6H_5CH_3$: Potassium bis(trimethylsilyl)amide (3.60 cm^3, 1.80 mmol) was added dropwise to a stirred solution of HFMes (0.50 g, 1.78 mmol) in THF (20 cm^3) at −30 °C. The resulting light yellow solution was stirred overnight after stirring for two hours at sustained low temperature. Filtration, removal of solution volatiles *in vacuo* and washing with cold (0 °C) toluene (3 × 5 cm^3) gave the product as a colourless powder. Extraction into fresh THF (*ca.* 15 cm^3) and placement at −10 °C yielded $\mathbf{1}\cdot C_6H_5CH_3$ as small colourless prisms (0.52 g, 85%), mp 195 °C (dec.). ^1H NMR (C_4D_8O, 193 K): δ 2.03 (br s, 6H, 2 Ar-CH_3), 2.15 (s, 12H, 4 Ar-CH_3), 2.17 (br s, 6H, 2 Ar-CH_3), 2.22 (s, 3H, Ar-CH_3), 2.27 (s, 3H, Ar-CH_3), 2.29 (s, 6H, Ar-CH_3), 2.32 (s, 3H, toluene-CH_3), 6.69 (s, 1H, NH), 6.73 (br s, 2H, η^6-*m*-H), 6.84 (br s, 2H, η^6-*m*-H), 7.18 (m, 3H, 3 toluene Ar-H), 7.19 (m, 2H, 2 toluene Ar-H), 7.21 (br s, 2H, non-η^6-*m*-H), 7.36 (br s, 2H, non-η^6-*m*-H), 8.22 (br s, 1H, NC(H)N FMes), 9.13 (br s, 1H, HFMes). ^{13}C NMR (OC_4D_8, 213 K): δ 19.2, 19.7 (br s, Ar-CH_3), 19.9, 20.1, 21.2, 21.2, 21.3, 21.8 (s, Ar-CH_3), 126.3, 129.3, 129.9, 131.5, 138.6 (s, Ar-C), 129.9, 135.8, 147.7,

150.33 (br s, Ar-C), 158.8 (s, NC(H)N HFMes), 182.5 (s, NC(H)N FMes). IR (Nujol) ν/cm^{-1}: 695sh s, 779m, 853m, 932m, 1007m, 1147s, 1213s, 1288s, 1550br s, 1633br s, 2389br m, 2728sh m, 3013s br. Anal. calc. for $C_{45}H_{55}KN_4$: C, 78.21; H, 8.02; N, 8.11. Found: C, 77.96; H, 8.01; N, 8.40%. 1.0 and 0.5 eq. potassium hydride, and 0.5 eq. potassium bis(trimethylsilyl)amide reactions carried out analogously in toluene–TMEDA and THF respectively.

§ Crystal data for **1**·$C_6H_5CH_3$: $C_{45}H_{55}KN_4$, $M = 691.03$, colourless needles, monoclinic, space group $C2/c$ (no. 15), $a = 41.735(8)$, $b = 10.191(2)$, $c = 23.027(5)$ Å, $\beta = 122.13(3)$, $V = 8293(3)$ Å^3, $Z = 8$, $F_{000} = 2976$, Nonius Kappa CCD, Mo-Kα radiation, $\lambda = 0.71073$ Å, $T = 150(2)$ K, 61834 reflections collected, 9437 unique ($R_{\text{int}} = 0.0727$). The structure was solved and refined using the programs SHELXS-97[27] and SHELXL-97[28] respectively. The program X-Seed[29] was used as an interface to the SHELX programs, and to prepare the figures. Final GooF = 0.923, $R1 = 0.0504$, $wR2 = 0.1318$, R indices based on 5766 reflections with $I \geqslant 2\sigma(I)$ (refinement on F^2), 501 parameters, 0 restraints. Lorentzian polarisation and absorption corrections applied, $\mu = 0.162$ mm^{-1}. CCDC reference number 184978. See http://www.rsc.org/suppdata/dt/b2/b204224j/ for crystallographic data in CIF or other electronic format.

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