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Heavier alkali metal complexes of the bulky alkyl ligand 2-(bis(trimethylsilyl)methyl)-6-methylpyridine: Crystal structures of $[\{6\text{-Me}(2\ \text{Pyr})\}(\text{Me}_3\text{Si})_2\text{CNa}(\text{pmdta})]$ and $[\{6\text{-Me}(2\text{-Pyr})\}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$

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Abstract

Reaction of the bulky pyridyl based ligand 6-Me(2-Pyr)$(\text{Me}_3\text{Si})_2$CH with ^{n}BuM (M = Na, K) in the presence of the N donors pmdta (*N*,*N*′,*N*′,*N*″,*N*″ pentamethyldiethylenetriamine) and tmeda (*N*,*N*,*N*′,*N*′ tetramethylethylenediamine) resulted in the formation and crystallisation of the heavy alkali metal complexes, $[\{6\text{-Me}(2\text{-Pyr})\}(\text{Me}_3\text{Si})_2\text{CNa}(\text{pmdta})]$, **1**, and $[\{6\text{-Me}(2\text{-Pyr})\}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$, **2**. Single crystal X-ray diffraction studies show the sodium complex, **1**, to be monomeric with a six coordinate metal centre, while the unsolvated potassium complex, **2**, is polymeric, involving repeating η^3 1-aza-allyl and allylic interactions of the pyridyl moiety with the potassium cation.
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1. Introduction

Due to their ability to deliver stable organometallic complexes displaying unusual metal oxidation states and bonding modes, amongst significant structural diversity, bulky ligands derived from trimethylsilyl substituted methylpyridines have been widely used in exploring the chemistry of both main group and transition metals [1–18]. The basic template of these ligands provides several attractive features for the synthetic and structural chemist; in conjunction with either 2- or 2,6-substitution of the pyridyl ring the number of Me_3Si groups can be varied altering the steric bulk and degree of kinetic protection afforded metal centres, the pyridyl nitrogen can provide stabilisation through internal coordination, and the ligand can electronically re-arrange to accommodate both σ and π metal–ligand bonding modes. Our earlier studies with $[(2\text{-Pyr})(\text{Me}_3\text{Si})_2\text{C}^-]$ [1,7,12–18] and $[(2\text{-Pyr})(\text{Me}_3\text{Si})\text{HC}^-]$ [19] have shown how the p-block and transition metals invariably have the metal σ-bonded to the substituted methyl C, with coordination of the pyridyl N, while the s-block metals display a greater variety in bonding modes revealing carbanionic, aza-allylic and amido complexes. A similar pattern has also been observed with $[6\text{-Me}(2\text{-Pyr})(\text{Me}_3\text{Si})_2\text{C}^-]$ (=R) [15] though to-date there have been no alkali metal complexes of this ligand structurally characterised. While a substantial amount of work has been directed at elucidating the structural arrangements in solvated and unsolvated Li complexes of $[(2\text{-Pyr})(\text{Me}_3\text{Si})_2\text{C}^-]$ [1,20], which could be reasonably extrapolated to those of $[6\text{-Me}(2\text{-Pyr})(\text{Me}_3\text{Si})_2\text{C}^-]$, the heavier alkali metals remain largely unexplored with the exception of the enamides derived from the monosilylated ligand, $[(2\text{-Pyr})(\text{Me}_3\text{Si})\text{HC}^-]$ [19].

In this paper we report the synthesis and full structural characterisation of sodium and potassium derivatives of $[6\text{-Me}(2\text{-Pyr})(\text{Me}_3\text{Si})_2\text{C}^-]$ (=R).

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2. Results and discussion

2.1. Synthesis and characterisation

Both complexes were formed from the initial equimolar reaction of the ligand, RH, with either ^{n}BuNa or ^{n}BuK in hexane at 0 °C and subsequent addition of one or two equivalents, respectively, of a multidentate N based donor. Thus, pmdta was added to $[RNa]_n$ and tmeda to $[RK]_n$ and the resulting pale brown suspensions heated before being filtered to produce yellow solutions of both. Yellow crystals of the sodium complex were obtained on refrigeration of the solution at 4 °C over 5 days while pale orange crystals of the potassium complex were grown by slowly cooling the solution from 60 °C. The crystals were isolated, washed, and characterised by single crystal X-ray diffraction, NMR and elemental analysis revealing the complexes to be $[\{6\text{-Me}(2\text{-Pyr})\}(Me_3Si)_2CNa(pmdta)]$, **1** (yield 82%), and $[\{6\text{-Me}(2\text{-Pyr})\}(Me_3Si)_2CK]_\infty$, **2**, (yield 62%) (see Scheme 1).

Interestingly, despite the addition of two equivalents of tmeda to the reaction mixture of RH and ^{n}BuK only the unsolvated potassium alkyl could be obtained as a crystalline solid. Typically, the reaction of organo-alkali complexes with protic ligands in the presence of a Lewis donor yields the metal alkyl complex incorporating the donor molecules. However, it is becoming increasingly clear that for the heavier alkali metal complexes in particular, that traditional covalent dative bonding from Lewis bases to the electropositive metal centres faces competition from interactions that were once considered weak or compensatory; that of π(arene) and agostic bonding [21–25].

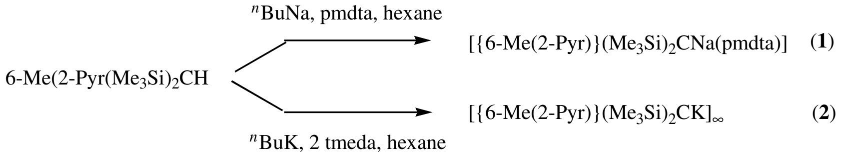
In light of this, further synthetic studies were conducted on the reaction with ^{n}BuK. When equimolar amounts of RH, ^{n}BuK and tmeda were reacted there was instant formation of a yellow solid. Following washing with hexane and in vacuo drying, ^{1}H NMR studies in C_6D_6 indicates that amongst a mixture the majority product is of the form $[RK^\cdot(tmeda)]_n$ [26]. However, no crystals of this complex could be obtained. When the RH:^{n}BuK ratio was increased to 2:1, a similar precipitate resulted, however, this isolated solid exhibited two ligand environments in the NMR, one protonated and one deprotonated, alongside one donor molecule, to yield a complex of the type $[RK(tmeda)(RH)]_n$ [26]. Heating the suspensions always resulted in crystals of **2** on slow cooling, as described above, and this was found to be the case irrespective of the reaction ratios employed. Therefore, the act of heating and slow cooling appears to favour the formation of the unsolvated polymeric potassium alkyl, which can be considered the most thermodynamically stable product. The insolubility of the $[RK]_n$ amorphous powder in hexane precludes the formation of crystalline **2** without the addition of tmeda.

2.2. X-ray structural determination

X-ray structure determination on single crystals of both revealed that the steric demands associated with the tridentate donor pmdta were significant enough to generate the monomeric sodium species $[RNa^\cdot(pmdta)]$, **1**, while tmeda was not incorporated into the potassium complex leaving the polymeric potassium alkyl $[RK]_\infty$, **2**.

Complex **1** crystallises in the monoclinic space group $P2_1/n$, with four molecules in the unit cell. Not surprisingly it is highly air and moisture sensitive, exhibiting a low melting range of 38–40 °C. The molecular structure of **1**, shown in Fig. 1, reveals a sterically crowded sodium centre, bonding with the three donor nitrogens of the pmdta as well as an η^3 1-aza-allyl interaction with the pyridyl nitrogen and carbon, and the carbon bearing the two Me_3Si substituents, causing the overall geometry about the metal centre to be distorted octahedral. The Na cation in the N–C–C–Na chelate system lies below the plane of the pyridine ring, exhibiting a wide range of interchelate ring bond angles from 53.5° to 122.0°. The terminal nitrogen atom, N(04), obtains the optimal orientation of the three donor pmdta nitrogens towards the metal centre, resulting in the shortest donor ligand to metal interaction. The pyridyl N–Na distance 2.38(1) Å is significantly shorter than the interactions for pmdta, 2.45(2)–2.59(2) Å, av. 2.53(2) Å with these latter distances being typical for tridentate coordinated pmdta to a Na^+ centre, e.g. $[BnNa(pmdta)\cdot 0.5(C_6H_6)]_\infty$ [27], 2.546(8)–2.655(8) Å, av. 2.584(8) Å, and those in $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$ [28] ranging from 2.47 to 2.58 Å. In contrast, larger N–Na distances of 2.609(3)–2.721(3) Å, av. 2.66 Å, are evident in the less crowded, dimeric complex $[PhNa(pmdta)]_2$ [29]. The pyridyl nitrogen to sodium bond length is comparable to those seen in the bidentate $[(bpy)^{2-}\{Na^+(pmdta)\}_2]$ [28] complex of 2.37–2.44 Å, av. 2.408 Å (see Table 1).

Comparative studies of alkali metal complexes [29] with the pmdta ligand have shown that N–metal–N (stereochemically determined) angles of 80–87° occur in organolithium compounds and 67–77° in organosodium compounds. Consistent with these findings are N–M–N bond angles of 73.5(7)° and 73.7(6)° corresponding to



Scheme 1. Synthetic routes to complexes **1** and **2**.

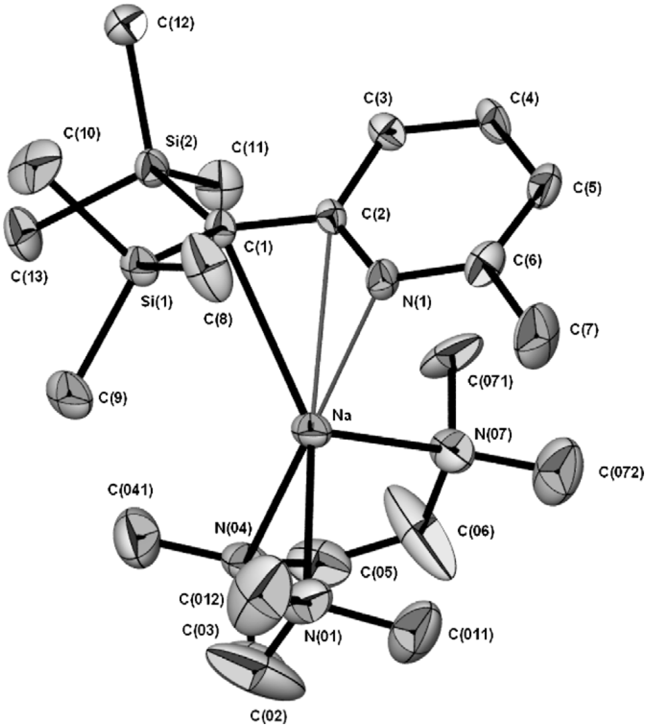


Fig. 1. Asymmetric unit of [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CNa(pmdta)], **1**. Thermal ellipsoids shown at 20% probability. All H atoms omitted for clarity. Selected bond lengths and angles given in Table 1.

N(01)–Na–N(04) and N(04)–Na–N(07). Due to the stereochemistry around the metal centre, the third N(01)–Na–N(07) angle of 106.9(6)° does not correlate with these values, but is comparable with the most obtuse N–M–N bond angle in [PhNa(pmdta)]$_2$ of 119.1(1)° (the remaining two being almost identical at 67.7° and 67.6°) [29].

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**

Na–N(1)	2.377(13)
Na –C(1)	2.838(14)
Na –C(2)	2.762(14)
Na–N(01)	2.55(2)
Na–N(04)	2.450(18)
Na–N(07)	2.594(15)
C(1)–C(2)	1.447(19)
N(1)–C(2)	1.28(2)
N(1)–Na–C(1)	53.5(4)
N(1)–Na–C(2)	27.6(5)
N(1)–Na–N(01)	118.7(6)
N(1)–Na–N(04)	167.2(6)
N(1)–Na–N(07)	97.6(5)
C(1)–Na–C(2)	29.9(4)
C(1)–Na–N(01)	138.9(5)
C(1)–Na–N(04)	120.8(6)
C(1)–Na–N(07)	114.0(5)
C(2)–Na–N(01)	142.8(6)
C(2)–Na–N(04)	142.1(6)
C(2)–Na–N(07)	96.8(5)
N(01)–Na–N(04)	73.5(7)
N(01)–Na–N(07)	106.9(6)
N(04)–Na–N(07)	73.7(6)

Complex **2**, isolated as a single crystalline product, crystallises as pale orange cubes in the monoclinic space group $P21/c$ (#14) with four molecules in the unit cell. When isolated from solution it is an extremely air and moisture sensitive, pyrophoric solid which decomposes at temperatures above 103 °C, and exhibits low thermal stability decomposing to a black solid over several weeks when stored under dry argon gas at room temperature. The linear polymer involves electrostatic $K^+ \cdots CR_3^-$ interactions, in an infinite chain-like structure.

The asymmetric unit, shown in Fig. 2, reveals two highly crowded potassium centres projecting behind and in front of the plane of the pyridine ring through C–K and N–K bonding. The figure is slightly misleading in that crystallographically the two K centres each have a site occupancy of 50%, thus maintaining charge balance. That the two metal environments are not identical is obvious from the infinite chain-like polymeric structure, shown in Fig. 3, which results from repeating η^3-aza-allyl and η^3-allyl interactions. The sandwiched pyridyl ring lies orthogonal between almost linear N–K–N and C–K–C interactions. Each link in the chain results in an almost 180° rotation of the pyridyl ring. While each potassium cation is formally six coordinate through bonding with the pyridyl system a 'pseudo' 10 coordinate metal centre is evident when taking into account the numerous agostic intra- and inter-molecular K···MeSi interactions (see Table 2).

There is a significant spread in the K–C bond lengths (range 2.874(4)–3.071(4) Å) between each K^+ centre and the pyridyl ring. The two shortest interactions of 2.881(2) and 2.890(2) Å are formed with the carbon atom in the ring adjacent to the pyridyl nitrogen. Delocalisation of negative charge around the pyridyl ring system and steric factors, produce stronger K–C interactions and subsequently shorter bond lengths. However, steric hindrance and repulsion from the Si atoms elongates the K–C bond length with the carbon bearing the two Me$_3$Si substituents to 3.027(4)

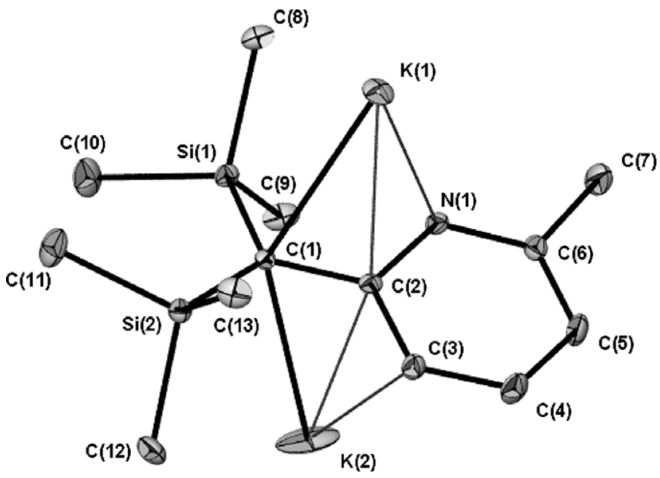


Fig. 2. Asymmetric unit of [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CK]$_\infty$, **2**. Thermal ellipsoids shown at 30% probability. All H atoms omitted for clarity. Selected bond lengths and angles given in Table 2.

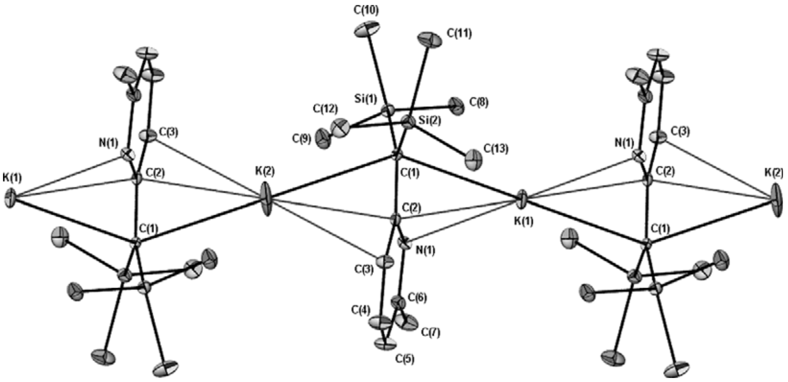


Fig. 3. Polymeric structure of $[\{6\text{-Me}(2\text{-Pyr})\}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$, **2**. Selected bond lengths and angles given in Table 2.

Table 2
Selected bond lengths (Å) and angles (°) for compound **2**

K(1)–N(1) #1	2.8223(19)
K(1)–C(2)#1	2.881(2)
K(1)–C(1)#1	3.023(2)
K(1)–C(1)	3.023(2)
K(2)–C(1)	3.037(2)
K(2)–C(2)#2	2.890(2)
K(2)–C(1)#2	3.037(2)
K(2)–C(3)#2	3.074(2)
K(1)–C(8)#1	3.148(2)
K(2)–C(9)#2	3.243(3)
N(1)–C(2)	1.387(3)
C(1)–C(2)	1.432(3)
C(2)–C(3)	1.436(3)
N(1)#1–K(1)–C(2)#1	28.12(6)
N(1)#1–K(1)–C(1)#1	48.67(6)
C(2)#1–K(1)–C(1)#1	27.94(6)
N(1)#1–K(1)–C(1)	131.33(6)
C(2)#1–K(1)–C(1)	152.06(6)
C(1)#1–K(1)–C(1)	180.0(1)
C(2)#2–K(2)–C(1)	152.18(6)
C(2)#2–K(2)–C(1)#2	27.82(6)
C(1)–K(2)–C(1)#2	180.0(1)
C(2)#2–K(2)–C(3)#2	27.64(6)
C(1)–K(2)–C(3)#2	130.79(6)
C(1)#2–K(2)–C(3)#2	49.21(6)
N(1)–C(2)–C(1)	117.96(19)

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

and 3.035(4) Å. Overall though they are shorter than those evident in $[(\text{Me}_3\text{Si})_3\text{CK}]_\infty$ [30], of 3.090(11) and 3.104(11) Å, and significantly shorter than the average in $[(\text{PhMe}_2\text{Si})_3\text{CK}]_\infty$ [30], 3.27 Å. The closest related structure is that of $[\text{Ph}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$ [31], which displays a similar polymeric structure to **2** though the shortest K–C distance of that to the benzylic carbon (3.007(2) Å) is still longer than the analogous bonds in **2**. The polymer, however, in this case is constructed primarily through the K cation being sandwiched between two benzylic units and forming an η^3-allylic (range 3.007–3.351(2) Å) connection to one and a η^6-phenyl interaction with the other (range 3.093(2)–3.522(2) Å). There is no observed rotation of the anionic moiety along the chain as seen in **2**.

These formally unsolvated K alkyls will also generally engage in compensatory agostic interactions to alleviate a low coordination environment around the metal centre. In this context we are using the term agostic to indicate primarily an electrostatic interaction between the metal cationic centre and the polarised C–H bonds rather than suggesting any degree of covalent electron sharing or multi-centred bonding [32]. The largely symmetrical nature of the interaction of the two K^+ cations with the numerous CH bonds in the two closest Me_3Si groups of **2** (for C8 and C9), precludes an analysis which would indicate significant geometrical changes in the anionic moiety resulting from such interactions. Previous studies on complexes which show Li···H–C agostic interactions [33], including on the close relative of **2**, $[(2\text{-Pyr})(\text{Me}_3\text{Si})_2\text{CLi}]_2$ [20], suggest an ambiguity in the source of close M···H–C contacts in that they may result simply from the preferred geometry of the anion rather than cause it. As with many other complexes which show close K···MeSi contacts [34] we can assume that the agostic bonds evident in **2** result from the size of ionic radius of the K cation, the formally low coordination environment of the metal ion in the unsolvated polymer, and the polarised nature of the Si–C–H bonds.

Since the precise locations of the H atoms were not observed on the difference map discussions on the relative bond distances involving agostic interactions by necessity centres on the closest C atoms rather than H. In **2** the K···MeSi interactions [K–C contacts 3.15, 3.24, 3.55, 3.63 Å, av. 3.39 Å] are longer in comparison with those in $[(\text{Me}_3\text{Si})_3\text{CK}]_\infty$ [30], (av. 3.23 Å) but are comparable with those in $[(\text{Me}_2\text{N})\text{Me}_2\text{Si}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$ [35], (av. 3.32 Å). $[\text{Ph}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$ [31] displays two types of agostic interactions: shorter intermolecular (K–C, av. 3.290 Å) and longer intramolecular (K–C, av. 3.550(3) Å) bonds. The K–N bond distance in **2**, 2.824(3) Å, is comparable with those observed in related unsolvated complexes, $[(\text{Me}_2\text{N})\text{Me}_2\text{Si}(\text{Me}_3\text{Si})_2\text{CK}]_\infty$, 2.848(1), and 2.812(5) Å, $[(\text{Me}_2\text{NMe}_2\text{Si})_3\text{CK}]_\infty$, 2.821(6) and 2.823(5) Å [35].

The linear C(1)–K–C(1)# bond angle of 180.0(1)° is similar to that exhibited by $[(\text{Me}_3\text{Si})_3\text{CK}]$ of 178.5°. There is a slight widening in the Si–C–Si bond angle, 125.7(2)°, in **2** when compared to the tris-silylated complexes

Table 3
Summary of crystallographic data for compounds **1** and **2**

	1	2
Chemical formula	$C_{22}H_{47}N_4Si_2Na$	$C_{13}H_{24}NSi_2K$
Formula weight	446.88	289.61
Crystal system	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/c$ (#14)
a (Å)	12.051(4)	9.834(2)
b (Å)	16.351(7)	18.322(4)
c (Å)	14.956(3)	10.026(2)
α (°)	90	90
β (°)	90.57(2)	110.14(3)
γ (°)	90	90
V (Å^3)	2947.0(2)	1696.1(6)
Z	4	4
T (K)	293	123
D_{calc} (g cm^{-3})	1.007	1.134
μ (cm^{-1})	1.50	6.86
$2\theta_{max}$ (°)	50	60.1
N_0 [$I > 2\sigma(I)$]	1534	2039
N unique	4575	4852
R, R_w	0.088, 0.103	0.063, 0.099
Goodness-of-fit	1.34	1.01

$[(PhMe_2Si)_3CK]$ [30], 118.0(2)°, $[(Me_2N)Me_2Si(Me_3Si)_2CK]_\infty$, av. 120.0°, and $[(Me_2NMe_2Si)_3CK]_\infty$, av. 119.8° [35]. Accompanying the wide C–Si–C bond angles are short C–Si bond lengths of 1.851(5) and 1.842(5) Å and marginally longer Si–Me contacts, av. 1.88 Å. The wide C–Si–C bond angles and short C–Si contacts are indicative of the highly ionic nature of **2** [35] (see Table 3).

2.3. Solution studies

Though **2** was only sparingly soluble in benzene both ^1H and ^{13}C NMR analyses were able to be carried out on both complexes. The spectra of **1** and **2** in C_6D_6 reveal the expected signals and splitting pattern for the substituted pyridyl ligand, and for **1** the additional pmdta ligand. The greater induced negative charge across the pyridyl ligand causes the protons in the Me_3Si groups to resonate at a lower frequency in **2** than observed for **1**, while the Me group and pyridyl protons appear at higher frequencies. Unfortunately, the inequivalent interactions of the metals on the protons of the Me_3Si protons are not apparent as these appear simply as singlets due to time average occupation at the temperature required for obtaining spectra in benzene (δ 0.52 in **1**, δ 0.16 in **2**). The greater charge polarisation in **2** relative to **1** is also indicated by the lower frequency resonance of the silylated pyridyl C^- in the ^{13}C NMR; δ 70.7 in **1**, δ 60.1 in **2**.

3. Conclusion

We have structurally characterised the first heavy alkali metal complexes of the bulky bis-trimethylsilyl 2,6-substituted pyridyl ligand [6-Me(2-Pyr)(Me$_3$Si)CH]. The interactions of the metal cations with the anionic moiety are through η^3 1-aza-allyl in both the monomeric pmdta solvated Na complex, with additional η^3 allylic interactions in the unsolvated polymeric K complex. This latter compound further demonstrates the relative strength of both metal – π interactions and electrostatic agostic interactions (K$\cdots$MeSi) in excluding the presence of any complexed Lewis donor molecules in the preference for forming a polymeric rather than solvated oligomeric structure in the crystalline state.

4. Experimental

4.1. General procedures

All compound manipulations were carried out under strict inert atmosphere and dry conditions using a vacuum/argon line, Schlenk techniques and a high purity argon gas recirculating dry box. Prior to use, solvents were dried by reflux over Na/K alloy and stored over molecular sieves 4 Å. [6-Me(2-Pyr)(Me$_3$Si)CH], **RH**, was prepared according to the literature procedure. ^{n}BuNa and ^{n}BuK were prepared from the metathesis reaction of ^{n}BuLi and ^{t}BuOM (M = Na, K) in hexane and stored as solids. (Note: these solids are extremely pyrophoric). Pmdta and tmeda were refluxed over CaH_2, distilled and stored over molecular sieve 4 Å. NMR spectra were obtained on Bruker AMX-300 spectrometer with chemical shifts referenced to the C_6D_6 solvent. Elemental analyses were carried out by CMAS, Australia.

4.1.1. Synthesis of [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CNa(pmdta)], *1*

6-Methyl-2-bis(trimethylsilyl)methylpyridine, {6-Me(2-Pyr)}(Me$_3$Si)$_2$CH}, (0.50 g, 1.98 mmol) was added slowly to a suspension of ^{n}BuNa (0.16 g, 2.00 mmol) in hexane (ca. 30 ml) at 0 °C and stirred for 30 min. Pmdta (0.35 g, 2.0 mmol) was added to the resulting suspension and the reaction mixture left to stir at ambient temperature for 12 h, which it was gently heated and filtered. The resulting solution was cooled to 4 °C yielding pale yellow crystals of **1** over 5 days.

Yield, 82%, m.p. 38–40 °C, ^1H NMR: (300.0 MHz, 25 °C, C_6D_6): δ 0.52 (18H, s, SiMe$_3$), 1.67 (12H, s, NMe$_2$), 1.98 (3H, s, N–Me), 2.14 (3H, s, Me) 6.01 (1H, m, H$_3$), 6.45 (1H, m, H$_5$), 6.90 (1H, m, H$_4$), ^{13}C NMR (75.0 MHz, 25 °C, C_6D_6): δ 5.5 (SiMe$_3$), 26.2 (C$_7$), 45.0 (NMe$_2$), 57.5 (NMe), 70.7 (C$_1$), 105.1 (C$_5$), 118.8 (C$_3$), 133. 8 (C$_4$), 149.2 (C$_6$), 154.3 (C$_2$). Anal. Calc. for $C_{22}H_{47}Si_2N_4Na$: C, 59.2; H, 10.6; N, 12.6. Found: C, 59.48; H, 10.92: N, 12.66%.

4.1.2. Synthesis of [{6-Me(2-Pyr)}(Me$_3$Si)$_2$CK]$_\infty$, *2*

6-Methyl-2-bis(trimethylsilyl)methylpyridine, {6-Me(2-Pyr)}(Me$_3$Si)$_2$CH}, (0.56 g, 2.20 mmol) was added slowly to a suspension of ^{n}BuK (0.43 g, 4.48 mmol) in hexane (ca. 30 ml) at 0 °C and stirred for 30 min. Tmeda (0.52 g, 4.48 mmol) was added to the suspension, which was then sonicated for 15 min to give a brown suspension. This suspension was warmed to just below boiling and placed in a Dewar of hot water (ca. 60 °C) and allowed to cool slowly to room temperature. This resulted in the formation of orange cubes of **2**.

Yield: 62%, m.p. > 103 °C (dec), ^{1}H NMR: (300 MHz, 25 °C, C_6D_6): δ 0.16 (18H, s, $SiMe_3$), 2.35 (3H, s, Me) 6.48 (1H, m, H_3), 7.01 (1H, m, H_5), 7.31 (1H, s, H_4), ^{13}C NMR (75.0 MHz, 25 °C, C_6D_6): δ 0.5 ($SiMe_3$), 31.0 (C_7), 60.1 (C_1), 117.4 (C_5), 119.8 (C_3), 135.6 (C_4), 146.5 (C_6), 153.9 (C_2). Anal. Calc. for $C_{13}H_{24}Si_2NK$: C, 54.1; H, 8.03; N, 4.85. Found: C, 52.60; H, 8.75; N, 4.79%.

4.2. Structure determinations

A single crystal of **1** was sealed in a glass capillary and data collected on a CAD4 diffractometer at 293 K using monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). A single crystal of **2** was coated in oil under argon in a dry box, mounted on a fibre and data collected on an Enraf–Nonius KappaCCD at 123 K with Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods (XTAL 3.4, SHELXS 97) and refined by full matrix least-squares on F^2 [36–38]. All H were placed in calculated positions (C–H 0.95 Å) and included in the final least squares refinement. All other atoms were located and refined anisotropically. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 295253 and 295254. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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