Synthesis and Structures of Alkali Metal Amides Derived from the Ligands $[N(SiMe_2Ph)(SiMe_3)]^-$, $[N(tBu)(SiMe_3)]^-$, $[N(Ph)(2\text{-}C_5H_4N)]^-$, and $[N(2\text{-}C_5H_4N)_2]^-$

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Dedicated to the memory of Ron Snaith

Keywords: Alkali metals / Amides / Synthesis / NMR spectra / X-ray structures

The following crystalline complexes are reported: $[(M\{\mu\text{-}N(SiMe_2Ph)(SiMe_3)\})_2]_n$ [the *cis* complex for $n = 1$ and M = Li (**1**); and the *trans* complexes with $n = \infty$ and M = Na (**2**), K (**4**), Rb (**5**), Cs (**6**)], $[(Na\{\mu\text{-}trans\text{-}N(SiMe_2Ph)(SiMe_3)\})_2(tmeda)]$ (**3**), $[(K\{\mu\text{-}trans\text{-}N(tBu)(SiMe_3)\})_4(\eta\text{-}C_6H_6)_2]$ (**7**), $[(K\{\mu\text{-}trans\text{-}N(Ph)(2\text{-}C_5H_4N)\})_2(\mu'\text{-}thf)_3]_\infty$ (**8**), and $[K\{\mu\text{-}N(2\text{-}C_5H_4N)_2\}]_\infty$ (**9**). Each, except **3**, was obtained by metallation of the appropriate secondary amine with Li*n*Bu (for **1**), MBzl [M = Na (for **2**), K (for **4** and **7**), Rb (for **5**), Cs (for **6**)], or KH (for **8** and **9**); treatment of **2** with an excess of tmeda yielded **3**. Each of **1**–**9** has an unusual, and in some cases unprecedented, molecular structure.

Introduction

Bulky alkali metal amides MNR_2 (especially M = Li and R = *i*Pr or $SiMe_3$, or NR_2 = 2,2,6,6-Me_4-piperidyl) are widely used as proton abstractors in organic synthesis, by virtue of their strong basicity but low carbon-centred nucleophilicity; and as reagents for the synthesis (including enantioselective) of compounds containing C−C bonds.[1−11] In coordination chemistry they are of synthetic interest as (i) ligand-transfer reagents; as substrates for (ii) reactions with protic compounds, thereby eliminating amine and generating new alkali metal compounds, and (iii) insertion of heterocumulenes or α-H-free organic cyanides.[12] They are also of major structural interest.[13−15]

We have a long-standing interest in the chemistry of metal and metalloid amides.[12] Many are prepared from the corresponding metal or metalloid chlorides, or other leaving groups such as triflates, by treatment with an alkali metal amide. Whereas lithium amides are the most readily available, the heavier alkali metal congeners, especially the sodium or potassium compounds, are often to be preferred because of the ease of separation of the target metal amide from the alkali metal halide coproduct.

Our most recent contributions have dealt with the crystalline dimeric dilithium diamide $[Li_2\{(1,3\text{-}CH_2NC_6H_3iPr_2\text{-}2',6')_2C_6H_4\}]_2$ [16] and crystalline polymeric lithium amides $[(Li\{\mu\text{-}N(Ph)R\}\text{-}trans)_2(\mu\text{-}tmeda)]_\infty$ (R = $SiMe_3$ or *t*Bu).[17]

Results and Discussion

Synthesis and Characterisation

In a preliminary communication, we described the conversion of $HN(SiMe_2Ph)(SiMe_3)$ into the crystalline lithium (**1**) and sodium (**2**) amides [as well as related chemistry based on $HN(Ph)SiMe_3$].[18] An objective was to compare their structures with those of the metal amides of the better known C_2-symmetric ligand $[N(SiMe_3)_2]^-$. In this paper we report (i) full details of the synthesis and characterisation of **1** and **2**; (ii) extensions to **3**, the crystalline tmeda complex of **2**, and the potassium (**4**), rubidium (**5**) and caesium (**6**) analogues of **1** and **2**; (iii) the synthesis of the potassium salt of another C_1-symmetric trimethylsilylamide $K[N(tBu)(SiMe_3)]$ **7a** and its crystalline benzene adduct **7**; (iv) the preparation of the crystalline potassium 2-pyridylamides $[K\{N(Ph)(2\text{-}C_5H_4N)\}\cdot 11/2thf]_\infty$ (**8**) and $[K\{N(2\text{-}C_5H_4N)_2\}]_\infty$ (**9**); and (v) X-ray structural data on the crystalline compounds **3**−**9** (those of **1** and **2** are in the literature[18]). As for (iv), the crystalline X-ray-characterised tmeda analogue of **8** $[K\{N(Ph)(2\text{-}C_5H_4N)\}(tmeda)]$ has been reported.[19] The first metal complexes of the ligand $[N(2\text{-}C_5H_4N)_2]^-$ to be described were the crystalline $[Cu_3\{N(2\text{-}C_5H_4N)_2\}X_2]\cdot H_2O$ chloride and bromide,[20] and further transition metal analogues have been much studied.[21]

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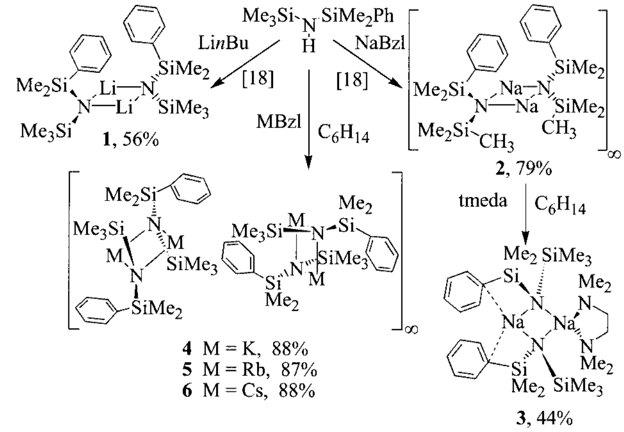


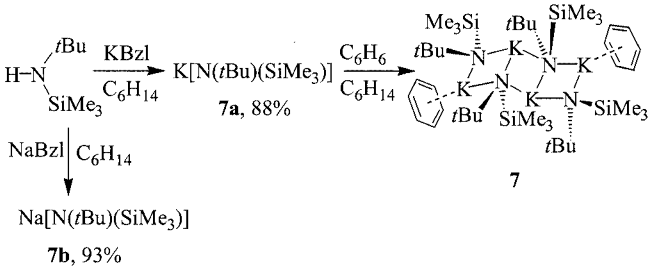
Scheme 1. Synthesis of the crystalline alkali metal phenyldimethylsilyl(trimethylsilyl)amides **1−6**; yields of **1−3** refer to X-ray quality specimens

The syntheses of the new alkali metal amides [(M{μ-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_n$ [n = 1 with M = Li (**1**); and n = ∞ with M = Na (**2**), K (**3**), Rb (**5**), Cs (**6**)], as well as that of the tmeda adduct **3** of **2**, are shown in Scheme 1. For each of **1**, **2**, **4**, **5**, and **6**, the parent silazane was metallated at −78 °C in hexane (**1**) or pentane, using *n*-butyllithium (**1**) or the appropriate heavier alkali metal benzyl (MBzl). The latter were prepared as solids from MO*t*Bu (M = Na, K, Rb), Li*n*Bu and toluene in hexane at −78 °C, the precipitated MBzl then thoroughly washed with hexane; CsBzl was obtained by carefully heating Cs in toluene at ca. 60 °C. Complex **3** was made from **2** and an excess of tmeda in hexane at ambient temperature, removal of volatiles and extraction of the residue with benzene; it is surprising that the dinuclear complex **3** contains only a single sodium-bound tmeda ligand.

The alkali metal amides **1**, **2**, **4**, **5** and **6** were found to be more soluble in hydrocarbon solvents than the corresponding compounds having the [N(SiMe$_3$)$_2$]$^-$ ligand, possibly in part due to the phenyl substituent assisting in delocalising the negative charge on the nitrogen atom. Each of the compounds **1−5** gave satisfactory microanalyses for hydrogen and nitrogen, although values for carbon were invariably low (as we have generally found for silicon-containing compounds, which is attributed to incomplete combustion). The caesium amide **6** proved to be too moisture-sensitive to give reproducible analytical data. Each of **1−6** gave satisfactory NMR and EI-mass spectra.

Treatment of trimethylsilyl(*tert*-butyl)amine with benzylpotassium, under identical conditions to those used for the preparation of **4**, yielded the potassium amide **7a** as a powder, which from benzene afforded the crystalline tetranuclear potassium amide as the bis(benzene) adduct **7** (Scheme 2). In a similar fashion, but using benzylsodium, the product was the sparingly hydrocarbon-soluble amorphous sodium amide **7b**, from which X-ray quality crystals were not obtained.

Values for ^{29}Si{^{1}H} NMR spectral chemical shifts in C$_6$D$_5$CD$_3$ for **1** or C$_6$D$_6$ for **2−6** and M[N(SiMe$_3$)$_2$] (M = Li, Na) at ambient temperature are shown in Table 1.



Scheme 2. Synthesis of the colourless solid sodium (**7b**) and potassium (**7a**) *tert*-butyl(trimethylsilyl)amides and the crystalline benzene adduct (**7**) of **7a**

Addition of *N*-2-pyridylaniline to potassium hydride in THF at ambient temperature yielded, after filtration and concentration of the filtrate, pale-yellow crystals of the corresponding potassium amide **8**, as a triply THF-bridging polymer of a tetranuclear array chain structure. The colourless, polymeric, crystalline bis(2-pyridyl)amidopotassium complex **9**, of layer structure, was obtained similarly, from bis(2-pyridyl)amine and KH in THF (Scheme 3). Each of the amides **8** and **9** was characterised by microanalyses (C, H, N) and ^{1}H and ^{13}C{^{1}H} NMR spectra in [D$_8$]THF, as well as their X-ray structures.

Crystal Structures

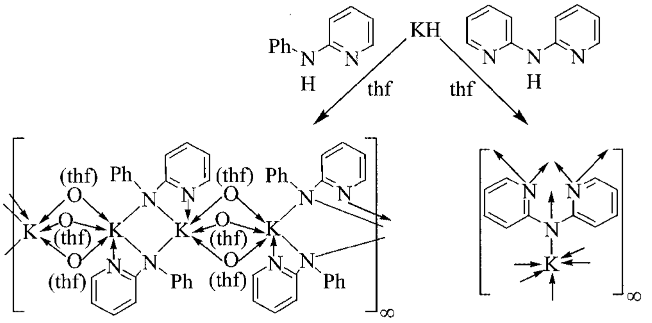
The structures of [Li{μ-*cis*-N(SiMe$_2$Ph)(SiMe$_3$)}]$_2$ (**1**) and [(Na{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (**2**) have been published.[18] In summary, **1** is unusual in that it appears to be only the second example of a neutral donor-free binuclear lithium amide,[18] albeit of opposite stereochemistry to that of [Li{μ-*trans*-N(C$_6$H$_3$*i*Pr$_2$-2,6)(SiMe$_3$)}]$_2$.[22] The LiNLi′N′ core in the C_2-symmetric **1**, unlike in the latter (which is centrosymmetric), deviates from a planar rhombus, the Li−N bonds ranging from 1.980(3) to 2.019(3) Å, the four atoms alternating above and below the plane by ca. 0.033 Å. The endocyclic angles subtended at the nitrogen atoms (71.75 ± 0.05°) are narrower than those at the lithium atoms (106.6 ± 0.3°), and are similar to those in [Li{μ-*trans*-N(C$_6$H$_3$*i*Pr$_2$-2,6)(SiMe$_3$)}]$_2$.[22] Crystalline **2** is a polymer of linked C_2-symmetric, planar dinuclear units, each attached to its neighbour by close Na···C contacts.[18] Neutral donor-free dinuclear sodium amides are, we believe, unprecedented. Each of **1** and **2** has close M···C contacts (see Table 9 below).

The crystalline dinuclear sodium amide − mono-tmeda adduct **3** is unusual in that the two four-coordinate sodium atoms of the central Na1N1Na2N2 core are in different environments: Na1 has an exocyclic chelating tmeda ligand, whereas Na2 has close Na2···C$_{ipso}$ contacts of 2.698 ± 0.006 Å (Figure 1); as a corollary, the endocyclic Na−N bonds are longer for Na1 than Na2 (Table 2) and both are significantly longer than those in **2** (2.420 ± 0.012 Å[18]) or in [Na{μ-*trans*-N(Ph)(SiMe$_3$)}(tmeda)]$_2$ (av. 2.475 Å[18]), while the endocyclic bond angle at N2 is much wider than that at N1 and their mean is close to that in **2** (102.2 ± 0.7 Å[18]).

Table 1. ^{29}Si{^{1}H} NMR spectral chemical shifts (δ) in C$_6$D$_6$ at 298 K of M[N(SiMe$_3$)$_2$] (M = Li, Na) and of compounds **1**−**7**

Compound	δ	Compound	δ
Li[N(SiMe$_3$)$_2$]	−10.7	[(K{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (**4**)	−24.0, −19.5
Na[N(SiMe$_3$)$_2$]	−14.5	[(Rb{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (**5**)	−[a]
[Li{μ-*cis*-N(SiMe$_2$Ph)(SiMe$_3$)}]$_2$ (**1**)	−13.9, −10.6	[(Cs{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (**6**)	−26.3, −21.8
[(Na{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (**2**)	−18.1, −13.2	K[N(*t*Bu)(SiMe$_3$)] (**7a**)	−18.2
[(Na{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$(μ-tmeda)] (**3**)	−20.9, −16.6	Na[N(*t*Bu)(SiMe$_3$)] (**7b**)	−25.4

[a] Not determined.



8, 89%, yellow

9, 93%, colourless

Scheme 3. Synthesis of the crystalline potassium 2-pyridylamides **8** and **9**

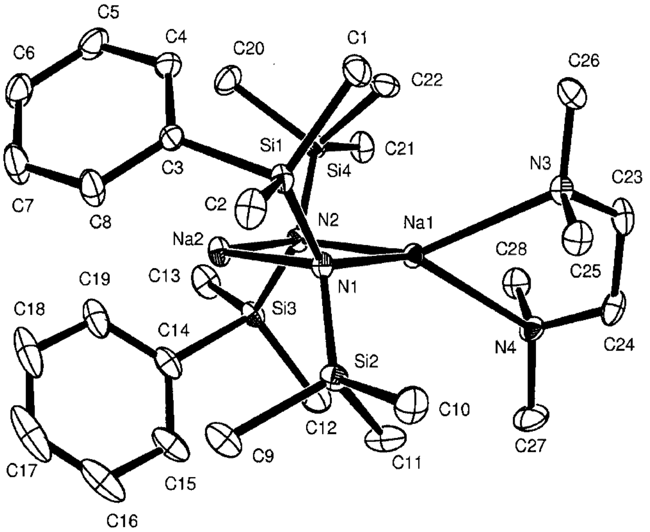


Figure 1. Molecular structure of [(Na{μ-*trans*-N(SiMe$_2$Ph)-(SiMe$_3$)})$_2$(tmeda)] (**3**)

Table 2. Selected bond lengths (Å) and angles (°) for **3**

Bond		Angles	
Na(1)−N(1)	2.5070(19)	N(1)−Na(1)−N(2)	97.50(6)
Na(1)−N(2)	2.5987(19)	N(3)−Na(1)−N(4)	69.23(7)
Na(1)−N(3)	2.624(2)	N(2)−Na(2)−N(1)	106.26(7)
Na(1)−N(4)	2.637(2)		
Na(2)−N(2)	2.387(2)		
Na(2)−N(1)	2.4118(19)		

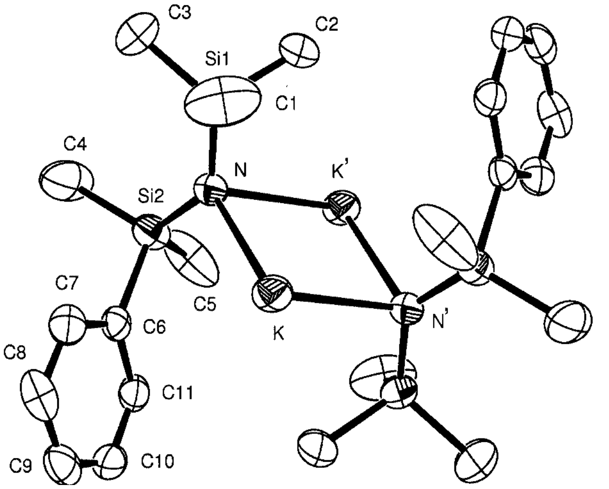


Figure 2. Molecular structure of [(K{μ-*trans*-N(SiMe$_2$Ph)-(SiMe$_3$)})$_2$]$_\infty$ (**4**), showing one of the dimeric units

Each of the crystalline alkali metal amides bearing the [N(SiMe$_3$)(SiMe$_2$Ph)]$^-$ ligand adopts a dinuclear structure. The heavier alkali metal amides [(M{μ-*trans*-N-(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (M = K, Rb, Cs) have a very similar crystal architecture. Two molecules are situated in the unit cell, which are orientated in such a way that the cations are stabilised by both intra- and intermolecular interactions with the methyl and/or phenyl substituents (Table 9), responsible for the polymeric aggregation. Descending the group, the [MN]$_2$ central core becomes progressively more rectangular.

X-ray quality crystals of [(K{μ-*trans*-N(SiMe$_2$Ph)-(SiMe$_3$)})$_2$]$_\infty$ (**4**) were obtained by sublimation at 180 °C and 5×10^{-4} Torr. The molecular structure of one dimeric unit is shown in Figure 2; there are two independent dimers **A** and **B** in the unit cell, each lying on an inversion centre. The phenyl groups in **A** are orthogonal to those in **B**. A list of selected interatomic bond lengths (Å) and angles (°) together with those of a related compound [K{μ-N(SiMe$_3$)$_2$}]$_2$ [23] are in Table 3. The structural parameters describing the internal core [KN]$_2$ in **4** are unexceptional. Comparing **4** with [K{μ-N(SiMe$_3$)$_2$}]$_2$,[23,24] only the Si(1)−N−Si(2) and SiB(1)−NB−SiB(2) [133.49(13) and 132.56(12)° [23]] angles show significant differences.

As shown by a portion of the structure of **4** depicted in Figure 3, close contacts between a potassium atom (say in **B**) and the phenyl ring of the neighbouring unit (say **A**) are present: [K−C(2) 3.512(2), K−C(3) 3.119(2), K−C(4)

Table 3. Selected bond lengths (Å) and angles (°) for **4** and $[K\{\mu\text{-}N(SiMe_3)_2\}]_2$ [23]

Bond or angle	**4 A**, [**B**]	Bond or angle	$[K\{\mu\text{-}N(SiMe_3)_2\}]_2$ [23]
K-N, [KB-NB]	2.778(2), [2.790(2)]	K−N	2.770(3)
K−N′, [KB-NB′]	2.808(2), [2.826(2)]	K−N′	2.803(3)
K−N−K′, [KB-NB-KB′]	83.59(6), [83.47(5)]	K−N−K′	85.53(9)
N−K−N′, [NB-KB-NB′]	96.42(6), [96.53(5)]	N−K−N	94.47(9)
Si(1)−N−Si(2), [SiB(1)−NB−SiB(2)]	133.49(13), [132.56(12)]	Si−N−Si′	129.18(18)

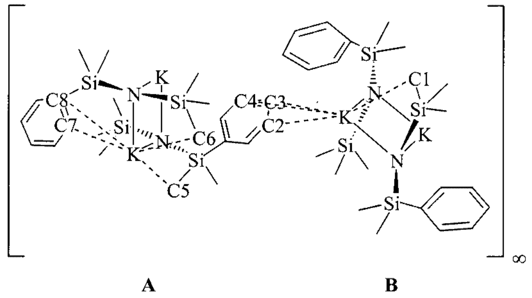


Figure 3. Schematic view of intra- and intermolecular K···C interactions in compound **4**

3.225(2) Å]. The same potassium atom is involved in an intramolecular K-methyl interaction, K−C(1), of 3.231(2) Å. In the other dimer (say **A**) the potassium atom has intramolecular contacts with the phenyl and methyl substituents: [K−C(5) 3.450(2), K−C(6) 3.357(2), K−C(7) 3.587(2) and K−C(8) 3.381(2) Å]. A higher coordination number with increasingly heavier alkali metal complexes is to be expected. The C_2-symmetric analogue $[K\{\mu\text{-}N(SiMe_3)_2\}]_2$ exhibits close intramolecular agostic-type contacts of 3.34 Å,[23] and also, as a referee (but not refs. 23 or 24) has noted, close intermolecular contacts.

Crystals of the rubidium amide **5** were obtained from a saturated toluene solution. There are two independent dimers **A** and **B** in the unit cell, as shown in Figure 4. A list of selected geometrical parameters for a single dimeric unit is shown in Table 4, together with comparative data for $[Rb\{\mu\text{-}N(SiMe_3)_2\}]_2$.[25] Crystalline **5** is similar to **4**, but the coordination sphere at the metal is different; thus the rubidium in the **A** molecule is involved in an η^6-bonding mode with the phenyl substituent of the **B** molecule [Rb−C(1B) 3.716(7), Rb−C(2B) 3.640(8), Rb−C(3B) 3.466(8), Rb−C(4B) 3.339(7), Rb−C(5B) 3.407(7), Rb−C(6B) 3.570(7) Å], as shown schematically in Figure 5.

Crystals of the caesium amide **6** were obtained from a solution in benzene and hexane. As for **4** and **5**, there are two independent dimers **A** and **B** in the unit cell, as shown in Figure 6. A list of selected geometrical parameters for a single dimeric unit is shown in Table 5, together with comparative data for $[Cs\{\mu\text{-}N(SiMe_3)_2\}]_2$ (**C**) and $[Cs\{\mu\text{-}N(SiMe_3)_2\}]_2(\mu'\text{-}\eta^6,\eta^6\text{-PhMe})]_\infty$ (**D**).[25] The caesium atom in each of **A** and **B** has a different coordination environment, as shown schematically in Figure 7. In **A**, there are two close intra-**A** and three inter-**A/B** Cs···Ph contacts: Cs−C(1) 3.473(2), Cs−C(2) 3.556(2), Cs−C(3) 3.682(2), Cs−C(4) 3.487(2), Cs−C(5) 3.586(2) Å. In **B**, only intra-**B**

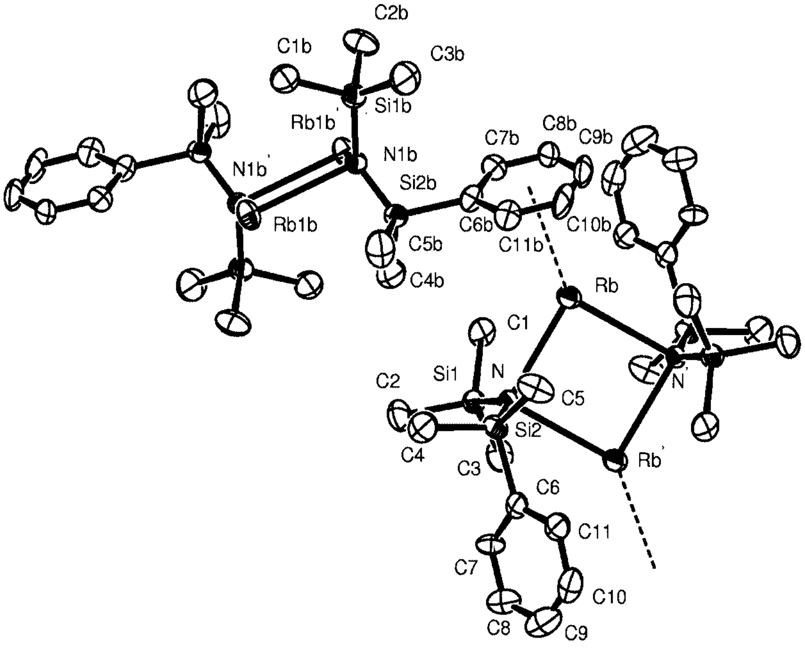


Figure 4. Molecular structure of $[(Rb\{\mu\text{-}trans\text{-}N(SiMe_2Ph)(SiMe_3)\})_2]_\infty$ (**5**), showing adjacent dimeric units

Table 4. Selected bond lengths (Å) and angles (°) for **5** and [Rb{μ-N(SiMe$_3$)$_2$}]$_2$ [23]

Bond or angle	**5 A**, [**B**]	Bond or angle	[Rb{μ-N(SiMe$_3$)$_2$}]$_2$ [23]
Rb−N, [RbB-NB]	2.898(6), [2.901(6)]	Rb−N	2.878(2)
Rb−N′, [RbB-NB′]	3.056(5), [2.914(6)]	Rb−N′	2.956(3)
Rb−N−Rb′, [RbB-NB-RbB′]	87.81(15), [85.56(17)]		
N−Rb−N′, [NB-RbB-NB′]	92.19(15), [94.44(17)]	N−Rb−N′	92.01(1)
Si(1)−N−Si(2), [SiB(1)−NB−SiB(2)]	133.1(4), [128.2(4)]	Si−N−Si′	130.7(1)

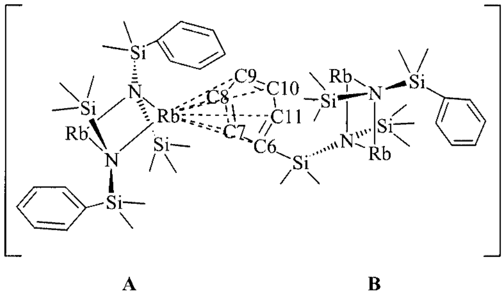


Figure 5. Schematic view of **5**, which highlights the Rb-phenyl contacts

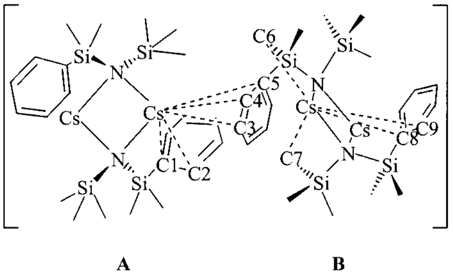


Figure 7. Schematic view of caesium-carbon contacts in a dimeric pair **A** and **B** of [(Cs{μ-*trans*-N(SiMe$_2$Ph)(SiMe$_3$)})$_2$]$_\infty$ (**6**)

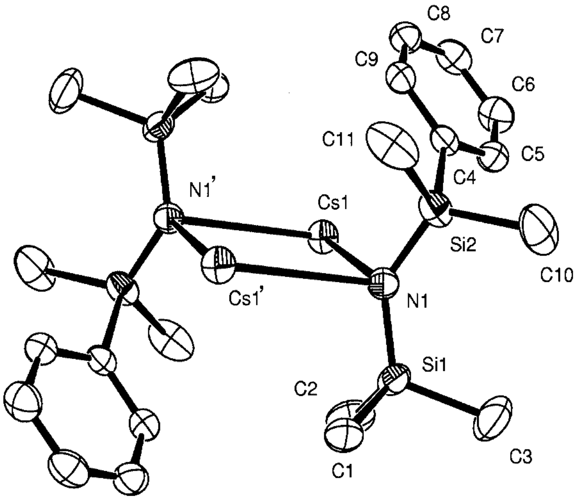


Figure 6. Molecular structure of [(Cs{μ-*trans*-N(SiMe$_2$Ph)-(SiMe$_3$)})$_2$]$_\infty$ (**6**), showing one of the dimeric units

Cs···Ph contacts are present: Cs−C(8) 3.451(2), Cs−C(9) 3.653(2) Å; but additionally there are two Cs···CH$_3$ close contacts: Cs−C(7) 3.624(2), Cs−C(6) 3.556(2) Å.

Compound **7** is a centrosymmetric tetramer, comprising a fusion of three rhomboidal planes, arranged in ladder fashion. The conformational order of the ladder in the molecule is *cisoid*-*transoid* with angles between the planes of 151.21° (Figure 8). The use of benzene as crystallisation solvent, which is η^6-coordinated to each terminal K$^+$ cation, may have caused the partial rupture of the probable infinite polymeric chain adopted by the solid [K{μ-N(*t*Bu)(SiMe$_3$)}]$_\infty$. We believe that **7** is the first oligomeric potassium amide having a ladder structure. The central rhomboid K2N2 K2′N2′ is flanked by terminal planar K1N1 K2N2 and K1′N1′K2′N2′ rings. The K2 and K2′ ions have three nitrogen atom neighbours and close K2···C3, K2′···C3′ contacts, while K1 and K1′ have two nitrogen neighbours and also are η^6-C$_6$H$_6$-bound. Selected bond lengths and angles are listed in Table 6, along with some comparative data for [K{μ-N(SiMe$_3$)$_2$}]$_2$.[23]

The crystalline complex [(K{μ-*trans*-N(Ph)(2-C$_5$H$_4$N)})$_2$(μ′-thf)$_3$]$_\infty$ (**8**) has a polymeric chain structure generated by alternation of inversion centres (relating N1 and N1′) and C_2 axes (through O3; Figure 9). Thus, the potassium ions in the chain are connected to one another by alternating bridges of three THF ligands (average K−O bond length, 2.79 Å) and two amido ligands (average K−NPh, 2.81 Å and average K−NC$_5$H$_4$, 2.90 Å). A similar [K-(μ-amido)]$_2$ motif is present in [K{μ-*trans*-[N(Ph)(2-C$_5$H$_4$N)]}(tmeda)]$_2$,[19] but the bridging is symmetrical [K−NPh, 2.805(3) Å; K−NC$_5$H$_4$-2, 2.841(2) and 2.877(3) Å]; in both this compound [K−N−K′, 73.9(1)° and

Table 5. Selected bond lengths (Å) and angles (°) for **6**, [Cs{μ-N(SiMe$_3$)$_2$}]$_2$ (**C**) and (**C**$_2$(μ′-η^6,η^6-PhMe)]$_\infty$ (**D**)

Bond or angle	**6 A**, [**B**]	Bond or angle	**C** [25]	**D** [25]
Cs(1)−N(1), [Cs(1B)−N(1B)]	3.199(2), [3.111(2)]	Cs−N	3.047(4)	3.016(2)
Cs−N′, [CsB-NB′]	3.200(2), [3.218(2)]	Cs−N′	3.149(2)	3.139(2)
Cs−N−Cs′, [CsB-NB-CsB′]	92.47(6), [94.74(5)]			
N−Cs−N′, [NB-CsB-NB′]	*av.* 91.13, [85.56]	N−Cs−N′	89.6(1)	90.71(1)
Si(1)−N−Si(2), [SiB(1)−NB−SiB(2)]	133.9(1), [132.69(1)]	Si−N−Si′	129.4(1)	128.02(1)

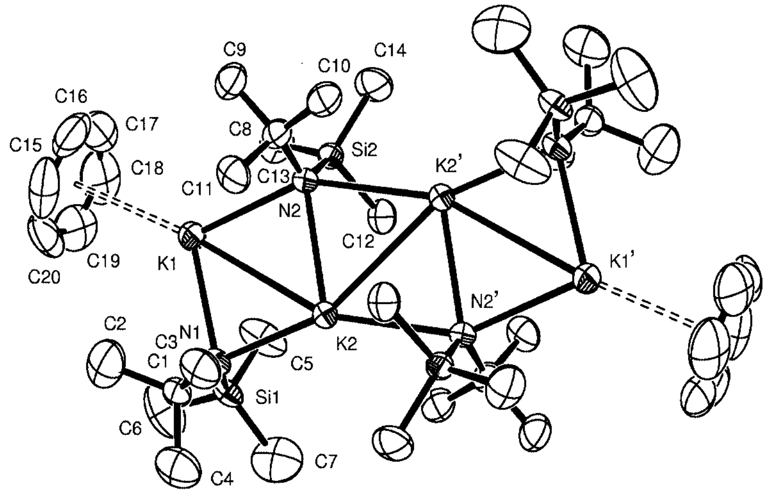


Figure 8. Molecular structure of [(K{μ-*trans*-N(*t*Bu)(SiMe$_3$)})$_4$(η-C$_6$H$_6$)$_2$] (**7**)

Table 6. Selected bond lengths (Å) and angles (°) for **7** and [K{μ-N(SiMe$_3$)$_2$}]$_2$ [23]

Bond or angle	**7**	[K{μ-N(SiMe$_3$)$_2$}]$_2$ [23]
K1−N1	2.726(2)	2.770(3)
K1−N2	2.934(2)	2.803(3)
K2−N1	2.701(2)	
K2−N2	2.821(2)	
N1−Si1	1.633(2)	1.678(3)
N2−Si2	1.616(2)	1.685(3)
K1−N1−K2	82.93(5)	85.53(9)
N1−K1−N2	98.15(5)	94.47(9)
N2−K2−N2′	107.10(4)	
K2−N2−K2′	72.89(4)	

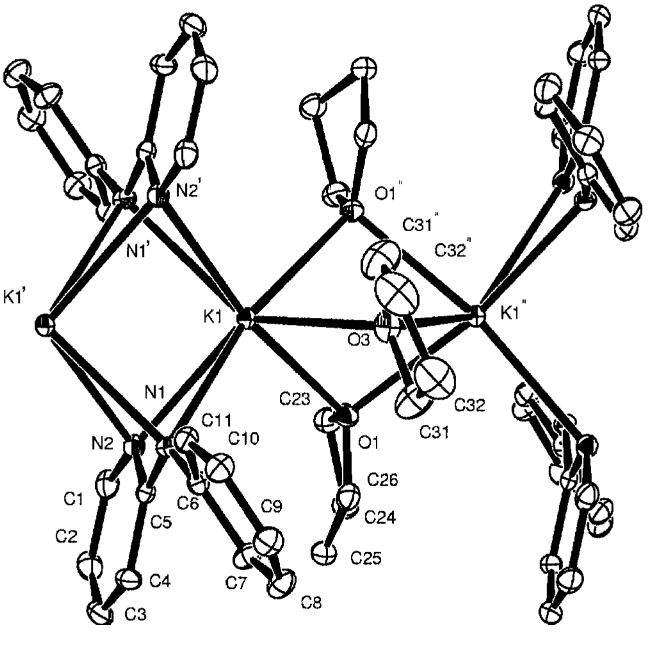


Figure 9. Polymeric chain crystal structure of [(K{μ-*trans*-N(Ph)(2-C$_5$H$_4$N)})$_2$(μ′-thf)$_3$]$_\infty$ (**8**)

N−K−N′, 106.0(1)°] and **8**, the central potassium amido KNK′N′ planar ring has comparable endocyclic bond angles. Similar endocyclic geometric parameters are also found in [K{μ-*trans*-[N(SiMe$_3$)(2-C$_5$H$_4$N)]}(12-crown-4)]$_2$ but the K-NSiMe$_3$ distances [2.858(2), 2.912(2) Å] are almost identical to the K−NC$_5$H$_4$-2 distance of 2.853(2) and 2.858(2) Å.[26] An unprecedented feature in the structure of **8** is the presence of the three bridging THF ligands in the M(μ-thf)$_3$M′ moiety; THF-bridging between two metals is well documented, as for M = K.[27−36] Table 7 lists selected geometric parameters for **8**.

Table 7. Selected bond lengths (Å) and angles (°) for **8**

Bond		Angles	
K(1)−O(1)	2.760(2)	O(1)−K(1)−O(1)′′	73.83(8)
K(1)−O(1)′′	2.817(2)	O(1)−K(1)−O(3)	77.48(6)
K(1)−O(3)	2.885(2)	O(1)′′−K(1)−O(3)	76.58(6)
K(1)−N(1)	2.836(2)	N(1)−K(1)−N(1)′	106.64(6)
K(1)−N(2)′	2.870(2)	N(2)−K(1)−N(2)′	106.90(6)
K(1)−N(2)	2.908(2)		
K(1)−N(1)′	2.924(2)		

The complex [K{μ-N(2-C$_5$H$_4$N)$_2$}]$_\infty$ (**9**) crystallises from THF as a THF-free polymer of layer structure (Figure 10); selected geometric parameters are given in Table 8. Complex **9** differs from each of **1**−**8** in being free from a central cyclic MNM′N′ core. Each potassium ion is in a six-coordinate KN$_6$ environment; for K, four of the nitrogen atoms (N2#1 and N2#2; N2#3 and N2#4) are from μ$_2$-bridging pyridine atoms on adjacent *cisoid* [N(C$_5$H$_4$*N*-2)$_2$]$^-$ ligands, while the other two are from μ$_2$-amido nitrogen atoms (N1 and N1#5) of another pair of *cisoid* [*N*(C$_5$H$_4$N-2)$_2$]$^-$ ligands. Each of the [N(C$_5$H$_4$N-2)$_2$]$^-$ ligands is thus hexadentate.

Conclusion

The synthesis and structures of the following crystalline alkali metal amides is reported:

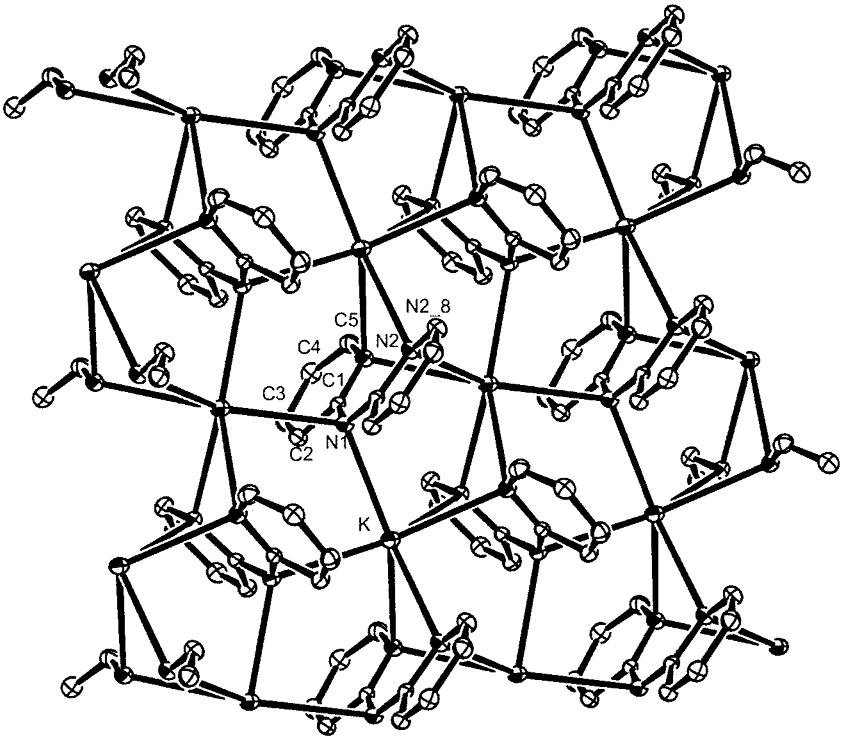


Figure 10. Polymeric layer crystal structure of $[K\{\mu\text{-}N(2\text{-}C_5H_4N)_2\}]_\infty$ (**9**)

Table 8. Selected bond lengths (Å) and angle (°) for **9**

Bond		Angle	
K−N(1)	2.8911(17)	N(1)−K−N(1)#5	84.62(3)
K−N(2)#1	2.8949(12)		
K−N(2)#2	2.8949(12)		
K−N(2)#3	2.9744(12)		
K−N(2)#4	2.9744(12)		
K−N(1)#5	3.0729(17)		

1. the homologous series of compounds $[(M\{\mu\text{-}N(SiMe_2Ph)(SiMe_3)\})_2]_n$ [the *cis* complex for $n = 1$ and $M = Li$ (**1**); and the *trans* complexes with $n = \infty$ and $M = Na$ (**2**), K (**4**), Rb (**5**), Cs (**6**)];
2. $[(Na\{\mu\text{-}trans\text{-}N(SiMe_2Ph)(SiMe_3)\})_2(tmeda)]$ (**3**);
3. $[(K\{\mu\text{-}trans\text{-}N(tBu)(SiMe_3)\})_4(\eta\text{-}C_6H_6)_2]$ (**7**);
4. $[(K\{\mu\text{-}trans\text{-}N(Ph)(2\text{-}C_5H_4N)\})_2(\mu'\text{-thf})_3]_\infty$ (**8**);
5. $[K\{\mu\text{-}N(2\text{-}C_5H_4N)_2\}]_\infty$ (**9**).

Each of **1−9** has an unusual, and in some cases unprecedented, molecular structure. Thus **1** is only the second example of a neutral donor-free binuclear lithium amide, while **2** has no antecedents as a neutral donor-free sodium amide. Complex **3** is remarkable in having only one of its two sodium ions bound by a chelating tmeda ligand. Each of the isoleptic amides **4**, **5** and **6** adopts a similar polymeric chain structure made up of a tetranuclear aggregate of two independent dimers **A** and **B**. The centrosymmetric tetranuclear potassium amide **7** is the first potassium amide of ladder structure. The polymeric chain complex **8** provides the first example of a complex in which two metal ions are bridged by three THF ligands. Complex **9**, although crystallised from THF, is a THF-free sheet polymer and is the first X-ray-characterised alkali metal bis(2-pyridyl)amide.

Table 9 provides a summary of the metal coordination environment, as well as M···L contacts, in which L represents a non-nitrogen-centred neutral ligand.

Experimental Section

General Remarks: All manipulations were performed under argon using standard Schlenk techniques. Toluene was dried using sodium. Pentane, benzene and hexane were dried using sodium-potassium alloy; THF was dried and distilled from sodium-benzophenone and stored over a sodium mirror under argon; tmeda (Aldrich) was distilled from CaH_2 prior to use. The NMR spectra were recorded on a Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C and 116.6 MHz for ^7Li) or AMX 500 (49.7 MHz for ^{29}Si) instruments and referenced externally (^7Li, using LiCl; ^{29}Si, using $SiMe_4$) or internally to the residual solvent resonances (chemical shift data in δ). Unless otherwise stated, all NMR spectra were measured at 298 K and other than ^1H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University. The amines $HN(tBu)SiMe_3$ and $HN(SiMe_2Ph)(SiMe_3)$ (Aldrich) were dried over KOH and distilled therefrom, while $HN(Ph)(2\text{-}C_5H_4N)$ and $HN(2\text{-}C_5H_4N)_2$ (Aldrich) were used without purification.

$[Li\{\mu\text{-}cis\text{-}N(SiMe_2Ph)(SiMe_3)\}]_2$ (1): LinBu (6 mL of a 1.6 mol·dm^{-3} solution in hexane, 9.60 mmol) was added dropwise to a cooled (−70 °C) and stirred solution of $HN(SiMe_2Ph)(SiMe_3)$ (2.13 g, 9.53 mmol) in pentane (35 mL) over a period of 15 min. The reaction mixture was warmed to room temperature and stirred

Table 9. Metal ligating atoms and coordination numbers (CN) and M···C close and K−O (**8**) contacts for compounds **1**−**9**

Compound	CN of M	M···Ph/ M···Me/ K···η^6-C_6H_6/ K−O/ Å
1	2N + C, 3	2.444(3) and 2.430(3), *ipso*-C.
2	2N +3C, 5	2.947(2) × 2, Me and 3.059(2), Me adjacent dimer.
	2N +4C, 6	2.868(1) × 2, *ipso*-C and 2.884(2) × 2, *ortho*-C.
3	2N +2C, 4	2.692(2), *ipso*-C and 2.730(3), *ipso*-C.
	4N, 4	
4	2N +4C, 6	3.381(2), *ipso*-C; 3.587(2), *o*-C; 3.450(2) and 3.357(2), Me.
	2N +4C, 6	3.512(2), *m*-C; 3.225(2), *m*-C; 3.119(2), *p*-C; 3.231(2), Me.
5	2N +6C, 8	3.339(7), *ipso*-C; 3.407(7), *o*-C; 3.466(8), *o*-C; 3.716(7), *m*-C; 3.640(8), *m*-C; and 3.570(7), *p*-C.
6	2N +5C, 7	3.473(2), *ipso*-C; 3.586(2), *ipso*-C; 3.556(2), *o*-C; 3.487(2), *o*-C; and 3.682(2), *m*-C.
	2N +4C, 6	3.451(2), *ipso*-C; 3.653(2), *o*-C; 3.556(2), Me; 3.642(2), Me.
7	2N +6C, 9	3.032, centroid of η-C_6H_6.
	3N +2C, 5	3.301(5) and 3.231(5), Me.
8	4N +3O, 7	2.760(2), 2.817(2) and 2.885(2), O
9	6N, 6	

for 12 h. The mixture was filtered and the filtrate was concentrated and stored at −25 °C for two days yielding tiny white crystals. Recrystallisation from hexane afforded colourless crystals of **1** (1.22 g, 56%), m.p. 60−65 °C. $C_{22}H_{40}Li_2N_2Si_4$ (458.8): calcd. C 57.6, H 8.79, N 6.10; found C 56.6, H 8.30, N 5.81. ^1H NMR ($C_6D_5CD_3$): δ = 0.02 (s, 9 H, $SiMe_3$), 0.27 (s, 6 H, $SiMe_2Ph$), 7.07−7.17 (m, 1 H, *p*-H), 7.20−7.25 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H), 7.45 (dd, $^3J_{H,H}$ = 6.4, $^4J_{H,H}$ = 1.4 Hz, 2 H) ppm. ^{13}C NMR ($C_6D_5CD_3$): δ = 3.5 ($SiMe_3$), 4.7 ($SiMe_2Ph$), 129.7, 129.9, 133.2, 143.8 (*ipso*-C) ppm. ^{29}Si NMR ($C_6D_5CD_3$): δ = −13.9, −10.6 ppm. ^7Li NMR ($C_6D_5CD_3$): δ = −2.0 ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 271 (10) $[M_2 - SiMe_2Ph - 3Me - Li]^+$, 208 (100) $[SiMe_2Ph + SiMe_3]^+$, 192 (57) $[271 - SiMe_3 - Li + H]^+$.

[(Na{μ-*trans*-N(SiMe₂Ph)(SiMe₃)})₂]∞ (2): Benzylsodium (0.43 g, 3.80 mmol) was added in small portions to a cooled (−78 °C) and stirred solution of $HN(SiMe_2Ph)(SiMe_3)$ (0.963 mL, 3.74 mmol) in hexane (50 mL). The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed at 35 °C/10^{-2} Torr for 30 min. The residue was washed with hexane to yield compound **2** as a white fluffy powder (0.72 g, 79%). $C_{22}H_{40}N_2Na_2Si_4$ (491.0): calcd. C 53.8, H 8.21, N 5.71; found C 52.5, H 8.28, N 5.49%. Recrystallisation from benzene after 1 day at 15 °C afforded colourless plates of **2** (0.57 g, 62%), m.p. 130−133 °C. ^1H NMR (C_6D_6): δ = 0.05 (s, 9 H, $SiMe_3$), 0.31 (s, 6 H, $SiMe_2Ph$), 7.14−7.23 (m, 3 H), 7.50 (d, $^3J_{H,H}$ = 7.7 Hz, 2 H) ppm. ^{13}C NMR (C_6D_6): δ = 5.1 ($SiMe_3$), 6.9 ($SiMe_2Ph$), 128.5 (*p*-C), 128.8, 132.7, 148.7 (*ipso*-C) ppm. ^{29}Si NMR (C_6D_6): δ = −18.1, −13.2 ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 342 (50) $[M_2 - PhSiMe_3 + 2H]^+$, 270 (55) $[Na_2M + 2H]^+$, 192 (100) $[M - Na]^+$, 135 (70) $[SiPhMe_2]^+$.

[(Na{μ-*trans*-N(SiMe₂Ph)(SiMe₃)})₂(tmeda)] (3): Addition of tmeda (0.57 mL, 3.75 mmol) to a milky suspension of $Na[N(SiMe_2Ph)(SiMe_3)]$ (0.46 g, 1.87 mmol) in hexane (40 mL) immediately gave a colourless mixture, which was stirred for 2 h at room temperature, then filtered. The volatiles were removed at 25 °C/10^{-2} Torr for 30 min. The residue was extracted with benzene (20 mL) and the extract was concentrated (to ca. 1 mL); hexane (10 mL) was added. Storage at −25 °C for two weeks yielded compound **3** (0.52 g, 44%) as transparent crystals, m.p. 55−60 °C. $C_{28}H_{56}N_4Na_2Si_4$ (607.1): calcd. C 55.4, H 9.30, N 9.22; found C 54.1, H 9.32, N 8.95. ^1H NMR (C_6D_6): δ = 0.23 (s, 9 H, $SiMe_3$), 0.47 (s, 6 H, $SiMe_2$), 1.52 (s, 4 H, CH_2, tmeda), 1.62 (s, 12 H, Me, tmeda), 7.23 (m, 3 H, *p*-H and *m*-H), 7.66 (d, $^3J_{H,H}$ = 7.77, $^4J_{H,H}$ = 1.37 Hz, 2 H, *o*-H) ppm. ^{13}C NMR (C_6D_6): δ = 5.3 ($SiMe_3$), 7.1 ($SiMe_2Ph$), 45.3 (CH_3, tmeda), 56.6 (CH_2, tmeda), 132.95, 128.1, 128.6 (Ph), 149.8 (*ipso*-C) ppm. ^{29}Si NMR (C_6D_6): δ = −20.9 ($SiMe_3$), −16.6 ($SiMe_2Ph$) ppm. MS (*M* denotes the monomer of **3**): *m*/*z* (%) = 530 (8) $[M_2 - Ph]^+$, 500 (13) $[M_2 - Ph - 2Me]^+$, 475 (63) $[M_2 - SiMe_2Ph - 3H]^+$, 459 (80) $[M_2\text{-}2SiMe_3]^+$, 399 (35) $[M_2 - \text{amine} - Me]^+$, 230 (100) $[M - \text{tmeda} - Me]^+$, 208 (95) $[M - \text{tmeda} - Na - Me]^+$, 192 (82) $[208 - Me]^+$, 58 (100) $[1/2\ \text{tmeda}]^+$.

[(K{μ-*trans*-N(SiMe₂Ph)(SiMe₃)})₂]∞ (4): Benzylpotassium (1.0 g, 7.68 mmol) was added in small portions to a cooled (−78 °C) and stirred solution of $HN(SiMe_2Ph)(SiMe_3)$ (2.1 mL, 8.06 mmol) in hexane (60 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The volatiles were removed at 35 °C/10^{-2} Torr for 30 min. The residue was washed with hexane (4 × 15 mL) to yield compound **4** (1.76 g, 88%) as a white fluffy powder, m.p. 131−135 °C. $C_{22}H_{40}K_2N_2Si_4$ (532.1): calcd. C 50.5, H 7.71, N 5.35; found C 48.7, H 7.81, N 5.35. Sublimation at 180 °C/5 × 10^{-4} Torr afforded a few X-ray quality crystals. ^1H NMR (C_6D_6): δ = 0.12 (s, 9 H, $SiMe_3$), 0.28 (s, 6 H, $SiMe_2Ph$), 7.18 (dd, $^3J_{H,H}$ = 1.50, $^4J_{H,H}$ = 1.37 Hz, 2 H), 7.23 (d, $^3J_{H,H}$ = 7.23 Hz, 2 H), 7.55 (dd, $^3J_{H,H}$ = 7.51, $^4J_{H,H}$ = 1.35 Hz, 2 H) ppm. ^{13}C NMR (C_6D_6): δ = 5.6 ($SiMe_3$), 7.2 ($SiMe_2Ph$), 127.8, 128.3, 133.1 (Ph) ppm. ^{29}Si NMR (C_6D_6): δ = −24.0, −19.5 ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 270 (22) $[M_2 - SiMe_2Ph - SiMe_3\text{-}3Me + H]^+$), 208 (100) $[SiMe_3 + SiMe_2Ph]^+$, 194 (72) $[208 - Me + H]^+$.

[(Rb{μ-*trans*-N(SiMe₂Ph)(SiMe₃)})₂]∞ (5): Benzylrubidium (0.23 g, 1.30 mmol) was added in small portions to a cooled (−78 °C) and stirred solution of $HN(SiMe_2Ph)(SiMe_3)$ (0.35 mL, 1.36 mmol) in hexane (25 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The volatiles were removed at 25 °C/10^{-2} Torr for 30 min. The residue was washed with hexane (4 × 5 mL) to yield compound **5** (0.35 g, 87%) as a grey fluffy powder. $C_{22}H_{40}N_2Rb_2Si_4$ (615.9): calcd. C 42.9, H 6.55, N 4.55; found C 39.8, H 6.59, N 4.49. Compound **5** was extracted into hot toluene (10 mL) and the extract was filtered; the filtrate was concentrated and stored at 15 °C for 12 h to afford tiny transparent crystals, m.p. 150−152 °C. ^1H NMR ($C_6D_5CD_3$): δ = 0.03 (s, 9 H, $SiMe_3$), 0.22 (s, 6 H, $SiMe_2Ph$), 7.12 (m, 3 H, *p*-H and *m*-H), 7.49 (dd, $^3J_{H,H}$ = 7.84, $^4J_{H,H}$ = 1.46 Hz, 2 H) ppm. ^{13}C NMR ($C_6D_5CD_3$): δ = 5.4 ($SiMe_3$), 7.2 ($SiMe_2$), 127.6, 128.2, 133.2 (Ph) ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 344 (10)

$[\{RbN\}_2(SiMe_3)_2]^+$, 270 (95) $[\{RbN\}_2(SiMe_3) - H]^+$, 208 (100) $[M - Rb - Me]^+$, 192 (85) $[M - Rb - 2Me]^+$.

$[(Cs\{\mu$-*trans*-$N(SiMe_2Ph)(SiMe_3)\})_2]_\infty$ (6): Benzylcaesium (0.49 g, 2.20 mmol) was added in small portions to a cooled (−78 °C) and stirred solution of $HN(SiMe_2Ph)(SiMe_3)$ (0.59 mL, 2.31 mmol) in hexane (40 mL). The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The volatiles were removed at 35 °C/10^{-2} Torr for 30 min. The residue was washed with hexane (4 × 10 mL) to yield compound **6** (0.67 g, 88%), as a cream fluffy powder, m.p. (decomp.) 125 °C. Compound **6** was extracted into hot toluene and the extract was filtered; the filtrate was concentrated and stored at room temperature for 12 h to furnish a few X-ray quality crystals. ^{1}H NMR (C_6D_6): δ = 0.19 (s, 9 H, $SiMe_3$), 0.39 (s, 6 H, $SiMe_2Ph$), 7.10 (m, 1 H, *p*-H), 7.18 (m, 2 H, *m*-H), 7.67 (d, $^3J_{H,H}$ = 6.02 Hz, 2 H, *o*-H) ppm. ^{13}C NMR (C_6D_6): δ = 5.4 ($SiMe_3$), 7.4 ($SiMe_2Ph$), 127.4, 128.05, 133.9 (Ph), 150.8 (*ipso*-C) ppm. ^{29}Si NMR (C_6D_6): δ = −26.3, −21.8 ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 355 (9) $[M_2]^+$, 281 (12) $[M_2 - SiMe_3]^+$, 208 (100) $[M_2 - Cs - Me]^+$, 192 (53) $[M_2 - Cs - 2Me]^+$, 133 (81) $[PhMe_2Si - 2H]^+$, 78 (67) $[SiMe_3]^+$.

$[(K\{\mu$-*trans*-$NtBu(SiMe_3)\})_4(\eta$-$C_6H_6)_2]$ (7): Benzylpotassium (0.59 g, 4.56 mmol) was added in small portions to a cooled (−78 °C) and stirred solution of $HNtBu(SiMe_3)$ (1.18 mL, 4.80 mmol) in hexane (45 mL). The reaction mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed at 25 °C/10^{-2} Torr. The residual cream solid was washed with hexane (4 × 10 mL). Filtration and drying of the residue for 30 min at 25 °C/10^{-2} Torr yielded $K[NtBu(SiMe_3)]$ (**7a**; 0.77 g, 88%), as a white powder. $C_7H_{18}KNSi$ (367.0): calcd. C 45.8, H 9.01, N 6.98; found C 43.8, H 8.71, N 6.50. X-ray-suitable crystals were obtained by dissolving $K[NtBu(SiMe_3)]$ (0.49 g) in a mixture of hexane (40 mL) and benzene (20 mL). The solution was concentrated and stored at 15 °C for seven days yielding compound **7** as a few transparent, plate-shaped crystals, m.p. 131−135 °C. ^{1}H NMR (C_6D_6): δ = 0.18 (s, 9 H, $SiMe_3$), 1.26 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (C_6D_6): δ = 7.8 ($SiMe_3$), 39.15 (*t*Bu), 52.4 (C, *t*Bu) ppm. ^{29}Si NMR (C_6D_6): δ = −25.4 ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 423 (3) $[M_2 + tBu]^+$, 281 (5) $[M_2 - tBu - 2Me + H]^+$, 222 (29) $[K_2M]^+$, 167 (40) $[K(NtBu)_2 - Me + H]^+$, 147 (50) $[222 - SiMe_3]^+$, 73 (83) $[SiMe_3]^+$.

$Na[NtBu(SiMe_3)]$ (7b): Benzylsodium (0.54 g, 4.76 mmol) was added in small portions to a cooled (−78 °C) and stirred solution of $HNtBu(SiMe_3)$ (0.96 mL, 5.01 mmol) in hexane (45 mL). The mixture was warmed to room temperature and stirred for 5 h. The volatiles were removed at 25 °C/10^{-2} Torr. The residual cream solid was washed with hexane (4 × 10 mL). Filtration and drying of the residue in vacuo for 30 min at 25 °C/10^{-2} Torr yielded compound **7b** (0.78 g, 93%), as a white powder, m.p. 185−187 °C. ^{1}H NMR (C_6D_6): δ = 0.19 (s, 9 H, $SiMe_3$), 1.21 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (C_6D_6): δ = 7.4 ($SiMe_3$), 39.0 (*t*Bu), 51.9 (C, *t*Bu) ppm. ^{29}Si NMR (C_6D_6): δ = −18.2 ppm. MS (*M* denotes the monomer): *m*/*z* (%) = 229 (8) $[M_2 - SiMe_3$-$2Me + 2H]^+$), 207 (10) $[229 - Na]^+$, 149 (12) $[207 - SiMe_2]^+$.

$[(K\{\mu$-*trans*-$N(Ph)(2$-$C_5H_4N)\})_2(\mu$-thf$)_3]_\infty$ (8): *N*-2-Pyridylaniline (0.51 g, 3.00 mmol) was added in small portions to a stirred suspension of KH (0.13 g, 3.22 mmol) in THF (100 mL). The light yellow suspension was stirred for 2 h and filtered. The filtrate was concentrated to yield pale-yellow crystals of compound **8**, which, after drying in a vacuum, gave $K\{N(Ph)(2$-$C_5H_4N)\}$ (0.56 g, 89%). $C_{11}H_9KN_2$ (208.3): calcd. C 63.4, H 4.35, N 13.45; found C 63.35, H 4.38, N 13.51. ^{1}H NMR ([D$_8$]THF): δ = 7.78 (ddd, $J_{6\text{-H},5\text{-H}}$ = 4.97, $J_{6\text{-H},4\text{-H}}$ = 2.23, $J_{6\text{-H},3\text{-H}}$ = 0.90, 1 H, *6-H* of 2-C_5H_4N), 6.96 (m, 4 H, *o-* and *m-H* of Ph), 6.89 (ddd, $J_{4\text{-H},3\text{-H}}$ = 8.76, $J_{4\text{-H},5\text{-H}}$ = 6.59, $J_{4\text{-H},6\text{-H}}$ = 2.23, 1 H, *4-H* of 2-C_5H_4N*)*, 6.71 (dt, $J_{3\text{-H},4\text{-H}}$ = 8.72, $J_{3\text{-H},5\text{-H}}$ = $J_{3\text{-H},6\text{-H}}$ = 0.99, 1 H, *3-H* of 2-C_5H_4N), 6.42 (m, 1 H, *p-H* of Ph), 5.83 (ddd, $J_{5\text{-H},4\text{-H}}$ = 6.35, $J_{5\text{-H},6\text{-H}}$ = 4.97, $J_{5\text{-H},3\text{-H}}$ = 1.05 Hz, 1 H, *5-H* of 2-C_5H_4N) ppm. ^{13}C NMR ([D$_8$]thf): δ = 166.6 (*ipso-C* of Ph), 156.4 (*2-C* of 2-C_5H_4N), 149.9 (*6-C* of 2-C_5H_4N), 136.0 (*4-C* of 2-C_5H_4N), 128.9 (*m-C* of Ph), 121.45 (*o-C* of Ph), 116.1 (*5-C* of 2-C_5H_4N), 107.9 (*3-C* of 2-C_5H_4N), 105.5 (*p-C* of Ph) ppm.

$[K\{\mu$-$N(2$-$C_5H_4N)_2\}]_\infty$ (9): Colourless complex **9** (0.46 g, 93%) was synthesised by a procedure similar to that used for compound **8**, from $HN(2$-$C_5H_4N)_2$ (0.40 g, 2.36 mmol), KH (0.10 g, 2.49 mmol) in THF (100 mL). $C_{10}H_8KN_3$ (209.3): calcd. C 57.4, H 3.85, N 20.08; found C 57.45, H 3.89, N 20.07. ^{1}H NMR ([D$_8$]THF): δ = 7.92 (d, *J* = 4.39 Hz, 2 H, *6-H*), 7.21 (d, *J* = 8.78 Hz, 2 H, *3-H)*, 7.09 (t, *J* = 8.78 Hz, 2 H, *4-H*), 6.14 (t, *J* = 5.86 Hz, 2 H, *5-H*) ppm. ^{13}C NMR ([D$_8$]THF): δ = 167.1 (*2-C* of 2-C_5H_4N), 149.0 (*6-*

Table 10. Crystallographic data for compounds **3−9** at *T* = 173(2) K

	3	**4**	**5**	**6**	**7**	**8**	**9**
Formula	$C_{28}H_{56}N_4Na_2Si_4$	$C_{22}H_{40}K_2N_2Si_4$	$C_{22}H_{40}N_2Rb_2Si_4$	$C_{22}H_{40}Cs_2N_2Si_4$	$C_{40}H_{84}K_4N_4Si_4$	$C_{34}H_{42}K_2N_4O_3$	$C_{10}H_8KN_3$
M	607.11	523.12	615.86	710.74	889.87	632.92	209.29
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	*Pnma* (No. 62)
a (Å)	11.3850(4)	13.5077(3)	11.4685(11)	11.5066(2)	10.9027(5)	23.705(2)	6.7598(3)
b (Å)	17.7048(6)	13.4679(2)	11.9751(12)	15.8809(4)	11.0047(4)	10.8276(10)	20.6744(14)
c (Å)	18.7964(4)	16.9813(3)	12.0417(9)	17.8558(4)	12.8942(5)	14.8147(9)	6.6776(4)
α (°)	90	90	82.850(5)	90	72.333(2)	90	90
β (°)	90.754(2)	99.365(1)	69.220(6)	106.499(2)	77.825(2)	115.378(5)	90
γ (°)	90	90	78.061(4)	90	65.383(2)	90	90
V (Å^3)	3788.4(2)	3048.1(1)	1510.4(2)	3128.5(1)	1333.73(9)	3435.5(5)	933.23(9)
Z	4	4	2	4	1	4	4
μ (mm^{-1})	0.20	0.48	3.41	2.49	0.45	0.31	0.53
Unique reflections, R_{int}	6661, 0.070	5336, 0.053	5269, 0.090	8942, 0.040	4560, 0.035	3007, 0.062	1388, 0.047
Reflections with $I > 2\sigma(I)$	4939	4524	2823	7692	3767	2011	1191
Final *R* indices	$R1 = 0.045$	$R1 = 0.038$	$R1 = 0.069$	$R1 = 0.033$	$R1 = 0.042$	$R1 = 0.051$	$R1 = 0.036$
$[I > 2\sigma(I)]$	$wR2 = 0.098$	$wR2 = 0.114$	$wR2 = 0.116$	$wR2 = 0.072$	$wR2 = 0.102$	$wR2 = 0.107$	$wR2 = 0.088$
R indices	$R1 = 0.072$	$R1 = 0.047$	$R1 = 0.157$	$R1 = 0.041$	$R1 = 0.055$	$R1 = 0.093$	$R1 = 0.045$
(all data)	$wR2 = 0.109$	$wR2 = 0.127$	$wR2 = 0.144$	$wR2 = 0.076$	$wR2 = 0.108$	$wR2 = 0.122$	$wR2 = 0.092$

C of 2-C_5H_4N), 135.95 (*4-C* of 2-C_5H_4N), 114.1 (*5-C* of 2-C_5H_4N), 109.45 (*3-C* of 2-C_5H_4N) ppm.

X-ray Crystallographic Study: Diffraction data for compounds **3−9** were collected on an Enraf−Nonius Kappa-CCD diffractometer using monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Crystals were directly mounted on the diffractometer under a stream of cold nitrogen gas. For compound **7**, the [N(*t*Bu)$SiMe_3$] groups are predominantly as shown in Figure 5 but with a small occupancy having the *t*Bu and $SiMe_3$ groups reversed; the disorder is 0.75:0.25 for the N1 group and 0.87:0.13 for the N2 group; the disorder was not resolved and hence the dimensions within these groups are unreliable. The structures were refined on all F^2 using SHELXL 97.[37] Further details are given in Table 10.

CCDC-209646 (**3**), -209647 (**4**), -209648 (**5**), -209649 (**6**), -209650 (**7**), -202589 (**8**), and -202590 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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