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Straightforward Synthesis of Rubidium Bis(trimethylsilyl)amide and Complexes of the Alkali Metal Bis(trimethylsilyl)amides with Weakly Coordinating 2,2,5,5-Tetramethyltetrahydrofuran

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**Keywords**: s-Block amides, Amides, Hexamethyldisilazanides, Bis(trimethylsilyl)amides, Tetramethyltetrahydrofuran Complexes

#### Abstract

Rubidium bis(trimethylsilyl)amide (rubidium hexamethyldisilazanide, Rb(hmds)) is accessible on large scale with excellent yields via a magnetite-catalyzed metalation of hexamethyldisilazane (H(hmds)) in liquid ammonia. Recrystallization of solvent-free alkali metal hexamethyldisilazanides [A(hmds)]<sub>n</sub> of sodium to cesium from solutions containing 2,2,5,5-tetramethyltetrahydrofuran (Me<sub>4</sub>THF, thf\*) yields the dinuclear complexes [(thf\*)A(hmds)]<sub>2</sub> which show a rather asymmetric coordination behavior of the bulky ether ligand with strongly bent A-A-O moieties for the heavier K, Rb, and Cs congeners whereas in the Na complex, the ether ligand is clamped between the trimethylsilyl groups. In hydrocarbon solutions, dissociation of these compounds is observed leading to liberation of this bulky and weakly binding cyclic ether.

#### Introduction

The amides of the alkali metals ANH<sub>2</sub> are well-known since many decades,<sup>1</sup> however, these compounds are salts that are insoluble in common organic solvents. Therefore, substituted amides are favored to enable homogenous reaction conditions and many derivatives are known, often commercially available and widely used in organic, metalorganic and coordination chemistry as metalation and amide transfer reagents.<sup>2</sup> Properties of these alkali metal amides can be influenced by the substitution pattern, neutral coligands (like ethers or amines) and the softness of the metal ions. The availability of alkyllithium offers a quantitative and straightforward access to lithium amides which often are prepared without the need to isolate the lithium amide for subsequent reactions. Therefore, it is not surprising that early reviews often focus on solid state<sup>3</sup> and solution structures<sup>4</sup> of lithium amides. Bulky amides,<sup>5</sup> especially the bis(trialkylsilyl)amides<sup>6</sup> and their congeners, guarantee small aggregation degrees and ensure solubility in common organic solvents, making these anions attractive in the coordination chemistry of the alkali metals. Especially lithium bis(trimethylsilyl)amide (lithium hexamethyldisilazide, Li(hmds)) has gained much attention due to its solubility and rich coordination and aggregation chemistry.<sup>7</sup> The organic amides of the heavier alkali metals<sup>8-10</sup> as well as mixed metal amides of the alkali metals<sup>11</sup> have gained interest only in recent years and also the bis(trimethylsilyl)amides of the heavy alkali metals have received only sporadic attention.<sup>12,13</sup> The presence of aromatic  $\pi$ -systems leads to additional intra- and intermolecular

2,2,5,5-Tetramethyltetrahydrofuran (Me<sub>4</sub>THF, THF\*) is a remarkable ether base because it combines an increased stability towards ether cleavage due to a protophilic attack by strong bases and shows a

interactions with the large and soft alkali ions.<sup>14</sup>

rather poor binding affinity.<sup>15</sup> This behavior is based on a lower basicity than tetrahydrofuran (THF)<sup>16</sup> and significantly enhanced bulkiness which allow the isolation and crystallization of unprecedented coligand-free tetranuclear  $[LiN(SiMe_3)_2]_4$  with an eight-membered  $Li_4N_4$  ring (Scheme 1).<sup>13</sup> However, in solution several species have been observed by NMR spectroscopy in analogy to earlier studies.<sup>4</sup> This unexpected observation initiated the investigation on the coordination behavior of this bulky ether at the heavier alkali metal bis(trimethylsilyl)amides (alkali metal hexamethyldisilazanides, A(hmds)).



**Scheme 1**: Preparation of solvent-free tetranuclear  $[Li(hmds)]_4$  ((1)<sub>4</sub>) via recrystallization of trinuclear  $[Li(hmds)]_3$  ((1)<sub>3</sub>) from 2,2,5,5-tetramethyltetrahydrofuran.

#### **Results and Discussion**

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Synthesis. Metalation of bis(trimethylsily)amine (hexamethyldisilazane, H(hmds)) allows the synthesis of the corresponding alkali metal hexamethyldisilazanides (A(hmds)). It's a frequent practice to prepare lithium bis(trimethylsilyl)amide with commercially available n-butyl lithium as metalation reagent (a, Scheme 2).<sup>17</sup> The sodium congeners are prepared by the use of sodium amide (b, Scheme 2), due to the lack of manageable sodium organyls.<sup>17a, 18</sup> Potassium bis(trimethylsilyl)amide is typically prepared using potassium hydride (c, Scheme 2) because potassium amide is sparsely listed by common chemical suppliers and furthermore, potassium hydride is easier to handle.<sup>19</sup> In some cases transmetalation with alkali metal alkoxides or metalation using benzyl potassium can be used.<sup>2</sup> Syntheses of the lighter s-block metal hexamethyldisilazanides are performed according to well established procedures, however, preparation of the heavier congeners rubidium and cesium are challenging. In both cases the metalation reagent is the metal itself, but surprisingly two of the strongest reducing agents of the periodic table of the elements  $(E^{0}(Rb/Rb^{+}) = -2,924 V; E^{0}(Cs/Cs^{+}) = -2,923 V)^{20}$  react very slowly with the moderately acidic amine hexamethyldisilazane ( $pk_a(H)$ hmds in THF = 25.8),<sup>21</sup> see Scheme 2 (d). In boiling amine reaction periods of several days are reported which favor undesirable side reactions, e.g. solvent degradation, leading to greenish solutions.<sup>22,23</sup> Recently, O'Hara and coworkers reported the amide transfer from lithium bis(trimethylsilyl)amide to cesium fluoride, avoiding elemental cesium (e, Scheme 2).<sup>12</sup> The synthetic protocol includes a number of preparative steps (salt metathesis in hexane, halide separation via solvent change to toluene, and final sublimation) and requires strict fulfilment of the reaction stoichiometry.

(a)	H-N(SiMe <sub>3</sub> ) <sub>2</sub> + <i>n</i> BuLi	- <i>n</i> BuH	[Li{N(SiMe <sub>3</sub> ) <sub>2</sub> }]
(b)	H-N(SiMe <sub>3</sub> ) <sub>2</sub> + Na(NH <sub>2</sub> )	- NH <sub>3</sub>	[Na{N(SiMe <sub>3</sub> ) <sub>2</sub> }]
(C)	$H-N(SiMe_3)_2 + KH$	- H <sub>2</sub>	[K{N(SiMe <sub>3</sub> ) <sub>2</sub> }]
(d)	$H-N(SiMe_3)_2 + A$	reflux, 2-10 d	[A{N(SiMe <sub>3</sub> ) <sub>2</sub> }]
(e)	[Li{N(SiMe <sub>3</sub> ) <sub>2</sub> }] + CsF	1. hexane 2. toluene, - LiF 3. sublimation	[Cs{N(SiMe <sub>3</sub> ) <sub>2</sub> }]

Scheme 2: Synthesis of alkali metal hexamethyldisilazanides.

We were interested in a straightforward synthesis of the heavier alkali metal hexamethyldisilazanides. Reaction of rubidium metal in diethyl ether with hexamethyldisilazane in the presence of liquid ammonia and catalytic amounts of magnetite Fe<sub>3</sub>O<sub>4</sub> allowed the synthesis in a multigram scale in excellent yields (97 %) and with short reactions periods. Condensation of ammonia in a rubidium metal / diethyl ether / hexamethyldisilazane suspension at -78 °C led to formation of rubidium bronze  $[Rb(NH_3)_x]$  which was well droplet separated (Figure 1) in contrast to the heavier alkaline earth metals forming one separate cohesive phase. Without addition of magnetite, the warm up of the reaction mixture led to boiling ammonia under decomposition of these bronze droplets. In contrast, addition of catalytic amounts of magnetite initiated the reaction of the rubidium bronze leading to a slightly blue colored reaction mixture (see Supporting Information, S1 c). At a temperature of -33 °C gas evolution occurred and slow warming to +30 °C led to complete consumption of the metal within 30 minutes. Thomson and Kleinberg investigated the oxidation of lithium metal in liquid ammonia and observed that the reaction and formation of lithium amide required the presence of oxygen gas which was bubbled through the reaction mixture or alternatively, oxygen saturated ammonia could be used yielding lithium amide and lithium peroxide.<sup>24</sup> These findings suggested that rubidium metal initially reacted to rubidium amide catalyzed by magnetite, followed by metalation  $(pK_h(NH_2^{-}) = -21)^{25}$  of hexamethyldisilazane  $(pk_a(H)hmds in THF = 25.8)^{21}$ , finally yielding rubidium bis(trimethylsilyl)amide according to scheme 3. Preliminary experiments using cesium metal underline that the described synthetic protocol is also applicable to the cesium congener.



Figure 1: Rubidium bronze in a mixture of diethyl ether and liquid ammonia at -78 °C.



**Scheme 3**: Reaction cascade yielding rubidium hexamethyldisilazanide in a one-pot synthesis involving liquid ammonia and catalytic amounts of magnetite.

Beside diverse preparation methods, solvent-free alkali metal hexamethyldisilazanides show a large structural variety in the solid state. Depending on the crystallization conditions, cyclic tri-<sup>26</sup> and tetranuclear<sup>13</sup> [Li(hmds)]<sub>n</sub> (n = 3, 4) is accessible. Two modifications, polymeric monoclinic<sup>27</sup> and cyclic trinuclear triclinic polymorphs,<sup>28</sup> are also known for crystalline Na(hmds). The hexamethyldisilazanides of the heavy alkali metals form dinuclear complexes of the type [A(hmds)]<sub>2</sub> with four-membered A<sub>2</sub>N<sub>2</sub> rings (A = K,<sup>29</sup> Rb,<sup>22</sup> and Cs<sup>22</sup>).

Recrystallization of coligand-free alkali metal hexamethyldisilazanides  $[A(hmds)]_n [A = Na ((2)_3), K ((3)_2), Rb ((4)_2), and Cs ((5)_2)]$  in the presence of 2,2,5,5-tetramethyltetrahydrofuran (THF\*) gave dinuclear  $[(thf*)A(hmds)]_2 [A = Na ((2 \cdot thf*)_2), K ((3 \cdot thf*)_2), Rb ((4 \cdot thf*)_2), and Cs ((5 \cdot thf*)_2)]$  with fourmembered  $A_2N_2$  rings and three-coordinate alkali ions as depicted in Scheme 4. Even though, thf\* is a significantly weaker Lewis base than thf, <sup>16</sup> adducts crystallize from saturated hydrocarbons.



**Scheme 4**: Synthesis of thf and thf\* complexes of the dinuclear alkali metal hexamethyldisilazanides of the type [(thf\*)A(hmds)]<sub>2</sub>.

*Crystallographic studies*. The molecular structures and numbering schemes of the [(thf\*)A(hmds)]<sub>2</sub> complexes of sodium (A = Na; (2·thf\*)<sub>2</sub>) and potassium (A = K; (3·thf\*)<sub>2</sub>) are depicted in Figures 2 and 3, respectively. The molecular structures of the rubidium (4·thf\*), and cesium (5·thf\*), derivatives are shown in the Supporting Information. Even though all these alkali metal derivatives exhibit rather similar structures (three-coordinate metal ions, four-membered A<sub>2</sub>N<sub>2</sub> rings), the distortion of the coordination spheres is evident. In the sodium complex (2·thf\*)<sub>2</sub> the bulky ether ligand fits well in coordination gap at the alkali ion and nearly linear Na2-Na1-O1 (176.45(5)°) and Na1-Na2-O2 alignments (177.80(5)°) are observed. The hmds and thf\* ligands adopt a propeller-like arrangement around the sodium atoms. Increasing size of the alkali metals leads to larger coordination sites. This effect is expressed by asymmetrical location of the thf\* ligand leading to strongly different proximal and distal N1/2-A1-O1 bond angles for the heavy congeners and bent A1A/A2-A1-O1 angles are observed for the potassium (158.87(3)°), rubidium (150.17(7)° and 155.41(6)°), and cesium derivatives (155.14(3)°). The larger coordination gap also allows a significantly more unstrained orientation of the thf\* molecules because they are not squeezed between the hmds ligands (leading to the propeller-like arrangement). Due to this fact intermolecular interactions dominate and the asymmetric coordination is mainly caused by the packing of the molecules in the crystalline state (see Supporting Information). Selected structural parameters are summarized in Table 1 in comparison to those of the cyclic coligand-free derivatives [A(hmds)]<sub>n</sub> as well as to the thf complexes  $[(thf)A(hmds)]_2$  of lithium  $((1\cdot thf)_2)^{22}$  sodium  $((2\cdot thf)_2)^{23}$  and potassium  $((3\cdot thf)_2)^{12c}$ 

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**Figure 2**: Molecular structure and numbering scheme of the  $[(thf*)Na(hmds)]_2$  complex  $((2 \cdot thf*)_2)$ . The ellipsoids represent a probability of 30 %, H atoms are neglected for clarity reasons. Selected bond lengths (pm): Na1-N1 245.31(16), Na1-N2 243.71(16), Na1-O1 242.80(15), Na2-N1 242.84(16), Na2-N2 244.91(16), Na2-O2 240.79(15), N1-Si1 169.24(15), N1-Si2 169.38(15), N2-Si3 169.40(15), N2-Si4 169.14(15); angles (deg.): N1-Na1-N2 100.12(6), N1-Na1-O1 133.75(6), N2-Na1-O1 126.09(6), N1-Na2-N2 100.47(6), N1-Na2-O2 128.03(6), N2-Na2-O2 131.30(6), Na1-N1-Na2 79.69(5), Si1-N1-Si2 123.62(9), Na1-N2-Na2 79.60(5), Si3-N2-Si4 126.50(9), Na2-Na1-O1 176.45(5), Na1-Na2-O2 177.80(5).



**Figure 3**: Molecular structure and numbering scheme of  $[(thf^*)K(hmds)]_2$  (**(K·thf^\*)**<sub>2</sub>). The ellipsoids represent a probability of 30 %, symmetry related atoms (-x+1, -y+1, -z+1) are marked with the letter A. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (pm): K1-N1 271.50(11), K1-N1A 288.01(11), K1-O1 271.40(9), N1-Si1 167.38(11), N1-Si2 167.51(12), angles (deg.): N1-K1-N1A 92.88(3), N1-K1-O1 112.25(3), N1A-K1-O1 153.18(3), K1-N1-K1A 87.12(3), Si1-N1-Si2 133.85(7), K1A-K1-O1 158.87(3).

With the increasing electropositive character and size of the alkali metal the ionicity of the A-N bonds increases. This fact leads to enhanced negative charge on the hmds ligand and to an increased back donation of charge from the nitrogen lone pair into the  $\sigma^*(Si-C)$  bond (negative hyperconjugation) resulting in a significant shortening of the Si-N bonds. These decreased bond lengths enhance steric repulsion between the rather bulky trimethylsilyl groups leading to large Si-N-Si bond angles.

Steric hindrance induced by the bulky thf\* ligands leads to a distortion of the A<sub>2</sub>N<sub>2</sub> rectangle and significantly different A-N bond lengths are formed for the complexes with the heavy alkali metals. The weaker basicity of thf\* and enhanced intramolecular steric repulsion compared to thf leads to a lengthening of the A-O bonds (as observed for the sodium complexes) or to smaller coordination numbers as found for the potassium derivatives. The comparison of [(thf\*)Rb(hmds)]<sub>2</sub> (av. Rb-O 292.1 pm) with [(thf)Rb(hmds)]<sub>2</sub> (Rb1-O1 283.8 pm) verifies a significant lengthening of the Rb-O bonds due to the weaker basicity of thf\*, intramolecular steric hindrance is not a structure-dominating factor due to the large radius of rubidium.

NMR Studies. Selected NMR parameters of the hexamethyldisilazanide complexes of [(thf\*)A(hmds)]<sub>2</sub> were recorded at  $[D_6]$  benzene solutions at room temperature and are listed in Table 2 showing characteristic trends like increasing high field shift of the <sup>29</sup>Si resonances and low field shifted  $\delta({}^{13}C{}^{1}H)$  values as the metal becomes more electropositive. However, <sup>1</sup>H DOSY NMR experiments verify that benzene is a competitive ligand to thf\* and hence, the ether ligands are substituted in benzene solutions and different diffusion coefficients are found for the hmds ligands and the thf\* molecules (Figure 4 and Supporting Information). In order to verify if the substitution of thf\* by benzene is responsible for the dissociation of the complexes [(thf\*)A(hmds)], we also dissolved the sodium congener as a representative example in a saturated alkane. Figure 4 shows the NMR spectra of sodium bis(trimethylsilyl)amide in  $[D_6]$  benzene (Figure 4, middle) as well as in  $[D_{12}]$  cyclohexane (Figure 4, bottom). In both cases, the tetramethyltetrahydrofuran molecules exhibit clearly different diffusion coefficients, verifying that a competitive Lewis base such as the soft  $\pi$ -system of the benzene molecule is not mandatory for this dissociation process. Instead, base-free alkali metal hexamethyldisilazanides dominate in solution whereas in the crystalline state, the thf\* adducts are preferred. This finding is based on entropic effects which play a negligible role in the solid ("frozen") state but the number of degrees of freedom in solution grows with the number of molecules; thus, three molecules (2 THF\* and [A(hmds)]<sub>2</sub>) are formed via complete dissociation of [(thf\*)A(hmds)]<sub>2</sub> (for the sodium complex, probably 6 THF\* and 2 [Na(hmds)]<sub>3</sub> molecules are formed via dissociation of three [(thf\*)Na(hmds)]<sub>2</sub> complexes). This observation supports that tetramethyltetrahydrofuran is a very weak Lewis base in the coordination chemistry of the alkali metals. For Li(hmds), thf\* adducts are neither known in the crystalline state nor in solution but tetrameric [Li(hmds)]<sub>4</sub> has been structurally authenticated when crystallization occurs in the presence of this bulky cyclic ether.

To verify the important role of  $\pi$ -coordination in the solvation of  $[(thf^*)A(hmds)]_2$  we solved  $[(thf^*)Cs(hmds)]_2((5\cdot thf^*)_2)$  in a mixture of  $[D_6]$  benzene / benzene (4:1) and the <sup>133</sup>Cs-<sup>1</sup>H-HOESY NMR spectrum (Figure 5) clearly verifies the ligand exchange forming benzene adducts of the type  $\{(benzene)_xA(hmds)\}$  (5·(C<sub>6</sub>H<sub>6</sub>)<sub>x</sub>)<sub>2</sub>.<sup>33</sup>

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**Figure 4**: NMR spectra of sodium bis(trimethylsilyl)amides at 297 K (400 MHz). The top <sup>1</sup>H NMR spectrum shows the resonance of Na(hmds) in [D<sub>6</sub>]benzene; in the middle the <sup>1</sup>H DOSY NMR spectrum of [(thf\*)Na(hmds]<sub>2</sub> dissolved in [D<sub>6</sub>]benzene is depicted. At the bottom the <sup>1</sup>H DOSY NMR spectrum of [(thf\*)Na(hmds]<sub>2</sub> in [D<sub>12</sub>]cyclohexane is shown (see text).



**Figure 5**: <sup>133</sup>Cs-<sup>1</sup>H-HOESY NMR spectrum of  $[(thf^*)Cs(hmds)]_2((5\cdot thf^*)_2)$  in a mixture of  $[D_6]$  benzene / benzene (4:1) at 297 K (400 MHz,  $\tau_m = 800$  ms).

**Table 2:** Selected NMR-parameters of the solvent free alkali bis(trimethylsilyl)amides ([A(hmds)]<sub>2</sub>,(2)<sub>3</sub>-(5)<sub>2</sub>), their dinuclear thf\*-adducts [(thf\*)A(hmds)]<sub>2</sub> ((2·thf\*)<sub>2</sub>-(5·thf\*)<sub>2</sub>) and their THF-adducts[(thf)A(hmds)]<sub>2</sub> ((2·thf)<sub>2</sub>-(4·thf)<sub>2</sub>) in [D<sub>6</sub>]benzene solution at room temperature (400 MHz).

Compo	und	δ( <sup>1</sup> H) [ppm]	δ( <sup>13</sup> C) [ppm]	δ( <sup>29</sup> Si) [ppm]	<sup>1</sup> J(Si,C) [Hz]	Lit.
(2)₃	•	0.10	6.94	-14.7	51.0	Here
(3)2	!	0.12	7.19	-20.5	53.8	Here
(4)2	!	0.17	7.25	-21.6	50.0	Here
<b>(5)</b> <sub>2</sub>	!	0.21	7.02	-22.2	49.6	Here
(2∙th	f) <sub>2</sub>	0.15	а	а	а	32
(3∙th	f) <sub>2</sub>	0.16	7.0	а	а	12c
(4∙th	f) <sub>2</sub>	0.17	6.88	-21.5	50.0	Here
(2∙thf	*)2	0.22	6.65	-14.6	51.5	Here
(3∙thf	*)2	0.14	6.83	-20.4	51.9	Here
(4∙thf	*)2	0.15	7.28	-21.6	51.2	Here
(5∙thf	*)2	0.20	7.30	-22.1	51.1	Here

<sup>a</sup>) These values are not reported in cited literature.

#### Conclusion

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The deprotonation of hexamethyldisilazane with rubidium and cesium metal in liquid ammonia requires many days and isolation of pure compounds is challenging. Addition of a very small amount

of magnetite accelerates this metalation and the formation of Rb(hmds) and Cs(hmds) significantly, allowing the preparation on a large scale with excellent yields.

2,2,5,5-Tetramethyltetrahydrofuran (thf\*) represents a very bulky cyclic ether with a weak Lewis basic character. Recrystallization of Li(hmds) in the presence of this ether leads to single crystals of tetrameric  $[Li(hmds)]_4$  ((1)<sub>4</sub>)with an eight-membered Li<sub>4</sub>N<sub>4</sub> ring. Repetition of this protocol with the heavier alkali metal hexamethyldisilazanides  $[A(hmds)]_n$  (A = Na, n = 3 and A = K, Rb, Cs, n = 2) allows to grow single crystals of dinuclear  $[(thf*)A(hmds)]_2$  (A = Na (2·thf\*)<sub>2</sub>, K (3·thf\*)<sub>2</sub>, Rb (4·thf\*)<sub>2</sub>, and Cs (5·thf\*)<sub>2</sub>) with four-membered A<sub>2</sub>N<sub>2</sub> rings. In the complex  $[(thf*)Na(hmds)]_2$  ((2·thf\*)<sub>2</sub>) with the rather small sodium atom, the bulky ether ligands are clamped between the large trimethylsilyl groups and intramolecular steric requirements lead to a propeller-like arrangement of the hmds and thf\* ligands. Increasing radii of the alkali ions lead to reduction of intramolecular steric strain and asymmetric binding behavior of the thf\* ligands is observed in the crystalline state due to intermolecular packing forces. Nevertheless, the weaker Lewis basicity of thf\* compared with thf leads to longer A-O distances regardless of steric strain.

In agreement with these observations in the solid state, dissociation of the complexes  $[(thf^*)A(hmds)]_2$  (A = Na (2·thf^\*)<sub>2</sub>, K (3·thf^\*)<sub>2</sub>, Rb (4·thf^\*)<sub>2</sub>, and Cs (5·thf^\*)<sub>2</sub>) in hydrocarbon solutions verifies the weak Lewis basicity of this cyclic ether. Dissociation in benzene can also be explained by a ligand exchange reaction because the  $\pi$ -system of benzene is a competitive Lewis base for large and soft metal ions. However, dissociation also occurs in aliphatic hydrocarbons like cyclohexane as has been demonstrated at the sodium derivative as an representative example for these alkali metal hexamethyldisilazanides.

In summary, bulky 2,2,5,5-tetramethyltetrahydrofuran forms complexes with the heavier alkali metal hexamethyldisilazanides which can be crystallized and isolated. In solution, nearly complete dissociation occurs and ether-free alkali metal hexamethyldisilazanides are observed.

#### Experimental

*General.* All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques, if not otherwise noted. The solvents were dried over KOH and subsequently distilled over sodium/benzophenone under a nitrogen atmosphere prior to use. Deuterated solvents were dried over sodium, distilled, degassed, and stored under nitrogen over sodium. <sup>1</sup>H, <sup>133</sup>Cs, <sup>29</sup>Si{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million relative to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si) or CsCl (<sup>133</sup>Cs) as an external standard referenced to the solvents residual proton signal. All substrates were purchased from Alfa Aesar, abcr, Sigma Aldrich or VWR and used without further purification. 2,2,5,5-tetramethyltetrahydrofuran was prepared by dehydration of 2,5-dimethyl-2,5-hexanediol with hydogenbromide solution (b.p. 117 °C).<sup>34</sup> Solvent-free Na(hmds) (**2**)<sub>3</sub> <sup>17a</sup> and Cs(hmds) (**5**)<sub>2</sub> <sup>23</sup> were prepared according to literature protocols. The yields refer to isolated crystalline compounds and are not optimized. Purity of the compounds was verified by NMR spectroscopy. The compounds were found to be too labile during weighing and handling to allow acquisition of consistent C,H,N analytical data.

*Rb(hmds)* (4)<sub>2</sub>: Rubidium metal (2.7 g, 31.5 mmol),  $Fe_3O_4$  (3 mg) and (H)hmds (7.3 mL, 34.8 mmol, 1.1 eq.) in diethyl ether (50 mL) were cooled to -78 °C in a SCHLENK-tube. About 7 mL of liquid ammonia was added to get a liquid rubidium bronze. The suspension was allowed to warm up under

vigorous stirring. At -30 °C the reaction starts and after 0.5 h the metal was fully consumed. The clear and colorless solution was allowed to warm to r.t. and stirred until gas evolution ceased. Diethyl ether was removed in vacuo and the remaining crystalline compound was dried in vacuum to isolate solvent-free Rb(hmds) (4)<sub>2</sub> (7.4 g, 30 mmol, 97%) as colourless powder. <sup>1</sup>H NMR (400 MHz. C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.17; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.25 (<sup>1</sup>J<sub>C,Si</sub> = 50.0 Hz); <sup>29</sup>Si-<sup>1</sup>H-DEPT NMR (79.41 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  - 21.56.

[(*thf*)*Rb*(*hmds*)]<sub>2</sub> (4·thf)<sub>2</sub>: colorless crystals; yield: 140 mg, 0.17 mmol, 47%; m.p.: 130°C (dec.); <sup>1</sup>H NMR (400 MHz. C<sub>6</sub>D<sub>6</sub>): δ 3.53 (m, 4H, CH<sub>2</sub>), 1.41(m, 4H, CH<sub>2</sub>), 0.17 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 67.4, 25.4, 6.9 (<sup>1</sup>J<sub>C,Si</sub> = 50.0 Hz); <sup>29</sup>Si-<sup>1</sup>H-DEPT NMR (79.41 MHz, C<sub>6</sub>D<sub>6</sub>): δ -21.54; IR (ATR) [cm<sup>-1</sup>]: 2937 (m), 2875 (m), 1232 (m), 1089 (s), 931 (m), 809 (vs).

General procedure for the synthesis of  $[(thf^*)A(hmds)]_2$ : A(hmds) (1-4 mmol, A = Na to Cs) was suspended in *n*-pentane (4 mL) in a SCHLENK-tube. Under vigorous stirring 2 eq. Me<sub>4</sub>THF was added dropwise until a clear solution was obtained. The solution was stored at -20 °C for 24 h leading to crystallization of ether adducts as colorless crystals. Separation and gentle drying in vacuum gives the  $[(thf^*)A(hmds)]_2$  complexes ((2·thf\*)<sub>2</sub>-(5·thf\*)<sub>2</sub>) as pure crystalline compounds in moderate yields.

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[(thf\*)Na(hmds)]<sub>2</sub> (2·thf\*)<sub>2</sub>: colorless crystals; yield: 636 mg, 2.0 mmol, 58%; m.p.:94 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.5 (s, 4H, CH<sub>2</sub>), 1.18 (s, 12H, CH<sub>3</sub>), 0.22 (s, 18H, H<sub>3</sub>CSi); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 81.3, 38.5, 29.7, 6.65 (<sup>1</sup>J<sub>C,Si</sub> = 51.5 Hz); <sup>29</sup>Si{<sup>1</sup>H} NMR (79.41 MHz, C<sub>6</sub>D<sub>6</sub>): δ -14.65; IR (ATR) [cm<sup>-1</sup>]: 2971 (m), 2944 (m), 2894 (w), 1244 (s), 1038 (s), 869 (s), 810 (vs), 654 (s).

[(thf\*)K(hmds)]<sub>2</sub> (**3·thf\***)<sub>2</sub>: colorless crystals; yield: 920 mg, 2.4 mmol, 82%; m.p.: 112 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.58 (s, 4H, CH<sub>2</sub>), 1.19 (s, 12H, CH<sub>3</sub>), 0.14 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>; <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 80.3, 38.6, 29.7, 6.8 (<sup>1</sup>J<sub>C,Si</sub> = 51.9 Hz); <sup>29</sup>Si NMR (79.14 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K): δ -20.45 (m); IR (ATR) [cm<sup>-1</sup>]: 2971 (m), 2936 (m), 2890 (w), 1107 (s), 992 (m), 875 (m), 806 (s), 647 )(m).

[(thf\*)Rb(hmds)]<sub>2</sub> (4·thf\*)<sub>2</sub>: colorless crystals; yield: 152 mg, 0.4 mmol, 50%; m.p.: 121 °C °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.57 (s, 4H, CH<sub>2</sub>), 1.17 (s, 12H, CH<sub>3</sub>),, 0.16 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 80.8, 39.0, 30.1, 7.3 (<sup>1</sup>J<sub>C,Si</sub> = 51.2 Hz); <sup>29</sup>Si-<sup>1</sup>H-DEPT NMR (79.41 MHz, C<sub>6</sub>D<sub>6</sub>): δ -21.55; IR (ATR) [cm<sup>-1</sup>]: 2937 (m), 2892 (m), 1380 (s), 1241(m), 1096 (s), 808 (vs).

[(thf\*)Cs(hmds)]<sub>2</sub> (5·thf\*)<sub>2</sub>: colorless crystals; yield: 222 mg, 0.5 mmol, 25%; m.p. 120 °C (dec.); <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 1.60 (s, 4H, CH<sub>2</sub>), 1.19 (s, 12H, CH<sub>3</sub>), 0.20 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>): δ 80.6, 39.0, 30.1, 7.3 (<sup>1</sup>J<sub>C,Si</sub> = 51.1 Hz); <sup>29</sup>Si-<sup>1</sup>H-DEPT NMR (79.14 MHz, C<sub>6</sub>D<sub>6</sub>, 297 K): δ -22.11; <sup>133</sup>Cs NMR (52.5 MHz, 297 K, C<sub>6</sub>D<sub>6</sub>): δ 130.51; IR (ATR) [cm<sup>-1</sup>]: 2966 (m), 2936 (m), 2888 (w), 1367 (m), 1311 (m), 1138 (s), 977 (m), 807 (vs).

*Crystallographic and refinement details*: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K<sub> $\alpha$ </sub> radiation. Data was corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans.<sup>35-37</sup> The structures were solved by direct methods (SHELXS)<sup>38</sup> and refined by full-matrix least squares techniques against  $F_o^2$  (SHELXL-97<sup>38</sup> and SHELXL-2014<sup>39</sup>). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, non-disordered atoms were refined anisotropically.<sup>38,39</sup> Crystallographic data as well as structure solution and

View Article Online DOI: 10.1039/C8DT01539B

refinement details are summarized in Table S1. XP (SIEMENS Analytical X-ray Instruments, Inc.)<sup>40</sup> was used for structure representations.

**Acknowledgement**: We thank Felix Pröhl for the synthesis of CsN(SiMe<sub>3</sub>)<sub>2</sub> and helpful discussions. Furthermore, we acknowledge the valuable support of the NMR (https://www.nmr.uni-jena.de/) and mass spectrometry service platforms (http://www.ms.uni-jena.de/) of the Faculty of Chemistry and Earth Sciences of the Friedrich Schiller University Jena, Germany.

# Supporting Information:

NMR and IR spectra of the reported compounds, molecule representation of the Rb and Cs derivatives, crystallographic and refinement details. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1838059 for (2·thf\*)<sub>2</sub>, CCDC-1838060 for (3·thf\*)<sub>2</sub>, CCDC-1838061 for (4·thf\*)<sub>2</sub>, CCDC-1838062 for (5·thf\*)<sub>2</sub>, and CCDC-1838063 for (4·thf)<sub>2</sub>. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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Table 1: Comparison of selected structural parameters of alkali bis(trimethylsilyl) amides without coligands, recrystallized from thf\*-containing solutions

([(thf\*)<sub>n</sub>A(hmds)]) and as tetrahydrofuran complexes ([(thf)<sub>n</sub>A(hmds)].

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	Agg. <sup>a</sup>	L	n	CN⁵	A-N	Si-N	A-L	N-A-N	O-A-N	Si-N-Si	Ref.
Li	Trimer	-	-	2	198.3-202.2	172.1-173.4	-	144.0-150.7	-	117.7-119.5	26b
Na	Trimer	-	-	2	237.7-240.4	169.6-170.2	-	136.9-142.8	-	125.3	28
К	Dimer	-	-	2	277.0	167.8, 168.5	-	94.5	-	129.2	29
Rb	Dimer	-	-	2	287.8, 295.6	167.7, 167.2	-	92.0	-	130.7	22
Cs	Dimer	-	-	2	307.4, 314.9	167.1, 167.4	-	89.6	-	129.4	22
Li	Tetramer	thf*	0	2	208.9	170.2	-	165.3	-	122.2	13
Na	Dimer	thf*	1	3	242.8-244.9	169.1-169.4	242.8, 240.8	100.1, 100.5	126.1-133.8	123.6, 126.5	Here
К	Dimer	thf*	1	3	271.5, 288.01	167.4-167.5	271.4	92.9	112.3, 153.2	133.9	Here
Rb	Dimer	thf*	1	3	284.4-310.7	166.8-168.0	289.7, 294.5	93.4	111.4-147.5	127.6, 128.4	Here
Cs	Dimer	thf*	1	3	300.3, 323.1	167.0, 167.1	310.0	92.0	113.2, 148.4	129.6	Here
Li	Dimer	thf	1	3	202.4	168.8	188.4	-	127.2	122.3	30
Na	Dimer	thf	1	3	239.9	167.5	226.7	101.7	128.1, 130.2	129.6	31
К	Dimer	thf	1	3+1 <sup>c</sup>	274.4, 285.3	167.1, 167.4	272.0	96.3	114.9, 129.7	127.1	12c
Rb	Dimer	thf	1	3	287.5, 298.8	167.2, 167.4	283.8	95.1	115.5, 129.4	129.1	Here

<sup>a</sup>) Aggregation degree (nuclearity of the molecular complex). <sup>b</sup>) Coordination number of the alkali metal A. <sup>c</sup>) Coordination number is enhanced by short contacts to the neighboring molecules leading to a polymeric network.

# **TOC** Picture



2,2,5,5-Tetramethyltetrahydrofuran (thf\*) is a very bulky cyclic ether with rather poor binding tendency due to weak basicity and steric hindrance. In the solid state, thf\* complexes are observed whereas in solution these complexes dissociate.

# **TOC Entry**

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