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Structural Studies of Cesium, Lithium/Cesium, and Sodium/Cesium Bis(trimethylsilyl)amide (HMDS) Complexes

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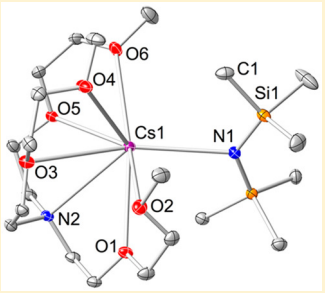
Supporting Information

ABSTRACT: Reacting cesium fluoride with an equimolar *n*-hexane solution of lithium bis(trimethylsilyl)amide (LiHMDS) allows the isolation of CsHMDS (**1**) in 80% yield (after sublimation). This preparative route to **1** negates the need for pyrophoric Cs metal or organocesium reagents in its synthesis. If a 2:1 LiHMDS:CsF ratio is employed, the heterobimetallic polymer $[LiCs(HMDS)_2]_\infty$ **2** was isolated (57% yield). By combining equimolar quantities of NaHMDS and CsHMDS in hexane/toluene $[toluene{\cdot}NaCs(HMDS)]_\infty$ **3** was isolated (62% yield). Attempts to prepare the corresponding potassium-cesium amide failed and instead yielded the known monometallic polymer $[toluene{\cdot}Cs(HMDS)]_\infty$ **4**. With the aim of expanding the structural diversity of Cs(HMDS) species, **1** was reacted with several different Lewis basic donor molecules of varying denticity, namely, (*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA] and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), tris[2-(dimethylamino)ethyl]-amine (Me_6-TREN) and tris[2-(2-methoxyethoxy)ethyl]amine (TMEEA). These reactions yielded dimeric $[donor{\cdot}NaCs(HMDS)_2]_2$ **5**−**7** [where donor is (*R*,*R*)-TMCDA, TMEDA and PMDETA respectively], the tetranuclear "open"-dimer $[\{Me_6\text{-}TREN{\cdot}Cs(HMDS)\}_2\{Cs(HMDS)\}_2]$ **8** and the monomeric [TMEEA·Cs(HMDS)] **9**. Complexes **2**, **3**, and **5**−**9** were characterized by X-ray crystallography and in solution by multinuclear NMR spectroscopy.



INTRODUCTION

Lithium secondary amides are among the most widely utilized reagents in modern synthesis. In particular, the "utility amides" lithium bis(trimethylsilyl)amide (LiHMDS), lithium diisopropylamide (LDA), and lithium 2,2,6,6-tetramethylpiperidide (LiTMP) are essential tools in most synthetic laboratories as non-nucleophilic strong Brønsted bases.[1] LiHMDS (most pertinent to this paper) itself has had a prominent role in organic synthesis.[2] Its utility is attributed not only to its Brønsted basic character, but also to the special profile of the TMS group, which makes LiHMDS soluble in a wide range of nonpolar organic solvents.[3] This and other features such as the lack of β-hydrogens[4] and the weaker basicity of LiHMDS compared to LiTMP and LDA [p*K* (LiHMDS) = 24.37; p*K* (LDA) = 35.41; p*K* (LiTMP) = 35.53][5] enables the facile isolation of reactive species, allowing access to structural models providing a basis for the clear understanding of structure/reactivity relationships.[6] In this context, the solution behavior of the alkali metal secondary amides of HMDS has focused primarily on the lithium salt [mainly using diffusion ordered spectroscopy (DOSY) techniques[7] and isotopically enriched $^6Li/^{15}N$ samples to deeply understand their aggregation state],[8] and the solid state structural chemistry of lithium, and its sodium congener have been reported in both the absence and the presence of synthetically important solvents. In 1969, Böttcher et al. reported the solid state structure of solvent-free LiHMDS, showing it existed as a LiN cyclotrimer.[9] This oligomer was discussed further in an Atwood et al. study 10 years later.[10] The solid state structure of NaHMDS was reported first by Grüning and Atwood as a polymeric chain of alternating N and Na atoms[11] and later by Nöth[12] and Driess[13] as a near-planar cyclotrimer. These compounds can behave as Lewis acids; the choice of donor solvent significantly affects the stabilization and final aggregation state of the complex. An increased reactivity is often noticed when a Lewis donor base is used in the reaction mixture, decreasing the aggregation state and increasing the solubility of the metal amide.[14] A review published in 2013 by Mulvey et al. highlights the structural chemistry of the known lithium, sodium, and potassium utility amides in the absence or in the presence of the most synthetically significant donor solvents[1] showing that a complex relationship exists between aggregation state and solvation. However, much less is known about the structural chemistry of heavier alkali metal HMDS bases, such as CsHMDS, in stark contrast to the increasing utility of this reagent in synthesis for metalation,[15] cyclization,[16] and nucleophilic trifluoromethylation reactions.[17] Our group recently published a study where CsHMDS is obtained as a byproduct, produced via salt metathesis involving NaHMDS and cesium halides and interacting with the ligand present in solution.[18] This absence of structural information may be due to the increased reactivity of heavier alkali metals and the considerable hazards involved with their synthesis. As well as CsHMDS,[19] other donor-free structurally characterized cesium secondary amide compounds, including salts of (trimethylsilyl)-

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(phenyldimethylsilyl)amide,[20] bis(diphenylphosphanyl)-amide,[21] 1,1-bis(trimethylsilyl)-2-phenylhydrazide,[22] carbazole,[23] and N(C_6F_5){C(CF_3)$_3$}, have been reported.[24] To the best of our knowledge, only six cesium salts of the aforementioned utility amides have been structurally characterized. Five of these contain HMDS[19,25] and one contains TMP.[26] Common protocols used to prepare heavy alkali metal amides include metathesis reactions of the corresponding lithium amide with heavier alkali metal alkoxides (i.e., NR_2Li + R′OM system)[27] and deprotonation of the amine with metallic alkali metal,[25c] alkali metal alkyl, aryl, hydride or alkoxide.[20,21] However, these methods have issues as they involve expensive reagents, many of which have to be synthesized or are extremely hazardous to manipulate. One of the most extensively used reactions involving alkali metal amides is the amide transfer reaction when an alkali metal amide reacts with metal halides (Scheme 1).[28]

Scheme 1. Alkali Metal Amides As Amide Transfer Reagents in the Presence of Metal Halides

$$n\,MNRR' + M'X_n \longrightarrow n\,MX + M'(NRR')_n$$

M = alkali metal M'= main group or transition element
X = halide R, R' = H, alkyl, aryl or substituted silyl

Salt metathesis using alkali metal halides is a common method employed for the synthesis of transition metals,[29] lanthanides,[30] and alkaline-earth metal amides.[3,31] However, to the best of our knowledge, this methodology has not been used before for the synthesis of heavy alkali metal amides. Here, we present a standardized protocol to safely prepare pure CsHMDS, not involving the risks associated with using cesium metal or organocesium reagents, avoiding decomposition related processes (i.e., metalation of solvents, etc. employed in the reaction) by using a CsF-salt metathesis approach. Our next objective was to prepare a series of heterobimetallic alkali metal complexes containing CsHMDS. Mixed alkali metal complexes have been found to offer enhanced reactivity over monometallic ones. For instance, Wittig reported that a 1:1 phenylsodium/phenyllithium mixture provided enhanced reactivity in the nucleophilic addition reaction toward benzophenone compared to homometallic derivatives (no reaction with phenyllithium).[32] Perhaps the most widely studied examples include the Lochmann−Schlosser superbase, which is a combination of *n*-butyllithium and potassium *tert*-butoxide (LiCKOR base).[33] This synergic "LiCKOR" system is a powerful metalating agent used in synthetic chemistry for deprotonation of a wide range of substrates.[34]

O'Shea has increased the interest in these type of heteroleptic complexes through his LiNK superbase system (LiTMP/KO^{t}Bu) which provides a different selectivity in metalation reactions of substituted benzylic substrates with respect to the Lochmann-Schlosser superbase system.[35] Since Williard's work in 1991,[36] few studies have included structural information relating to the chemistry of homoleptic hetero-alkali-metal utility amide species (these reagents can display enhanced deprotonative ability,[37] as shown by other mixed alkali metal organic formulations). This paper details our study on mixed-alkali metal/HMDS complexes in the solid state and in solution, as well as our investigations on donor complexes of CsHMDS.

RESULTS AND DISCUSSION

Synthesis. The focus of this work was to provide structural insight into heteroalkali metal/HMDS compounds as well as donor aggregates of homometallic CsHMDS. A primary goal was to develop a safe and efficient method for the synthesis of the key reagent, CsHMDS, in particular, to negate the need for utilizing Cs metal.

CsHMDS **1** was synthesized by treating anhydrous cesium fluoride with a *n*-hexane solution of LiHMDS [itself prepared *in situ* via deprotonation of HMDS(H) with *n*-BuLi] to undergo a salt metathesis reaction (Scheme 2). This implies a 1:1 metal

Scheme 2. Synthesis of Cesium Bis(trimethylsilyl)amide, Avoiding the Use of Cesium Metal

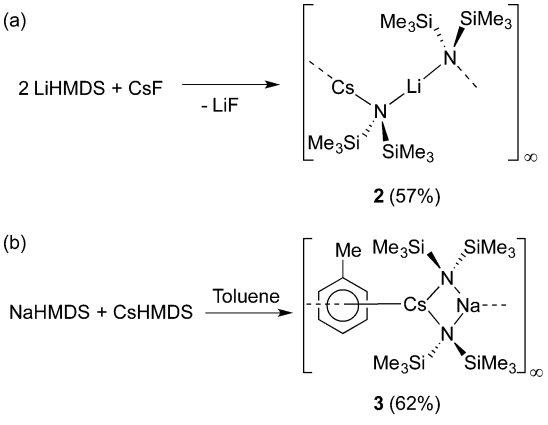
$$LiHMDS + CsF \xrightarrow[\text{ii) - LiF, toluene}]{\text{i) }\Delta\text{, }n\text{-hexane}} \underset{\mathbf{1}\ (80\%)}{CsHMDS}$$
iii) sublimation

interchange reaction, i.e., CsHMDS and formation of LiF. A precipitate was obtained by refluxing the reaction mixture for 15 h, and after removal of the solvent *in-vacuo*, toluene was added to the reaction mixture to dissolve the cesium amide (LiF is insoluble in toluene). The reaction was filtered to yield a colorless solution. The final product **1** appeared as a white crystalline solid[25c] in a good yield (80%) after sublimation. The product is stable under inert argon atmosphere for several months.

Following our success in the preparation of CsHMDS using the cesium halide route, the material was then utilized in the preparation of mixed-alkali metal amide reagents. The combination of CsHMDS with lithium reagents was attempted first as the difference in size between the alkali metals helped to combat issues related to mutual substitution disorder, observed when similarly sized alkali metals are present within a structure.[38]

The initial reaction involved a synthetic route similar to that for **1**. A *n*-hexane solution of LiHMDS was reacted with cesium fluoride, this time in a 2:1 LiHMDS/CsF molar ratio for 8 h at 68 °C. This synthetic route led to the preparation of a heterobimetallic lithium/cesium containing polymer [LiCs-(HMDS)$_2$]$_\infty$ **2** in moderate yields from a *n*-hexane/toluene mixture (57% yield based on the consumption of CsF) (Scheme 3a).

Scheme 3. Syntheses of (a) [LiCs(HMDS)$_2$]$_\infty$ 2 and (b) [toluene·NaCs(HMDS)$_2$]$_\infty$ 3



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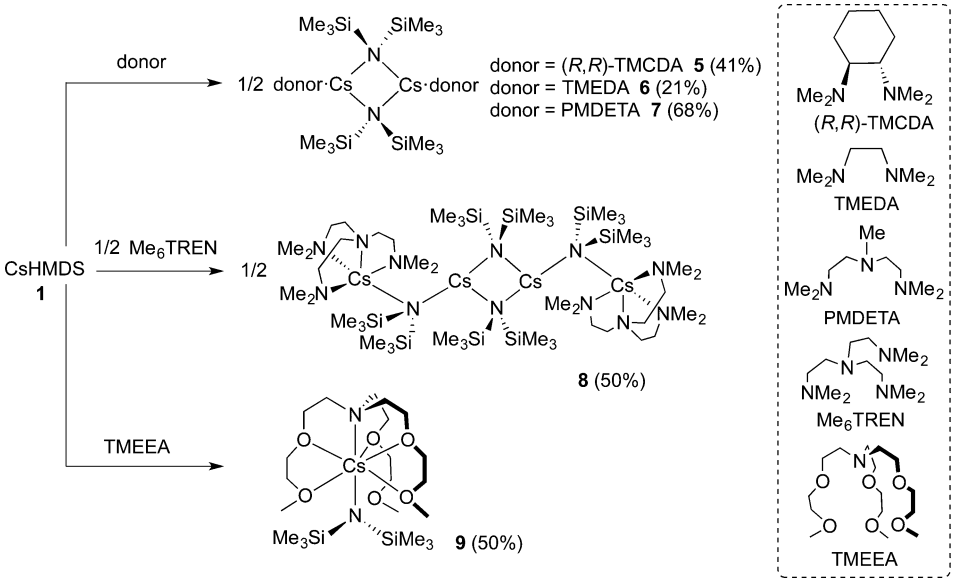
Scheme 4. Syntheses of [donor·CsHMDS]$_2$ [donor = (*R*,*R*)-TMCDA for 5, TMEDA for 6 and PMDETA for 7], [{Me$_6$-TREN·Cs(HMDS)}$_2${Cs(HMDS)}$_2$] 8, and [TMEEA·CsHMDS] 9



Because of the success of this reaction, it was decided to try to prepare a mixed-alkali metal aggregate containing sodium and cesium. A different synthetic approach was adopted and involved the combination of equimolar amounts of the homometallic reagents NaHMDS and CsHMDS in a hexane/toluene mixture, allowing the isolation of the mixed sodium–cesium amide polymer [toluene·NaCs(HMDS)$_2$]$_\infty$ **3** (isolated yield, 62%) (Scheme 3b).

Attempts to prepare a K/Cs hetero-bimetallic complex by reacting the monometallic amide species in a 1:1 ratio led to the preparation of an all cesium polymer [toluene·(CsHMDS)$_2$]$_\infty$ **4** previously reported in the literature.[19]

With the aim of providing additional structural insight in the aggregation behavior of CsHMDS (thus far only a discrete dimer and a few polymeric aggregates are reported in literature),[19,25b,c] the influence of the denticity of Lewis base donors on the formation of CsHMDS containing aggregates was studied. The initial donors selected were the bidentate ligands (*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA] and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA). By combining CsHMDS and the corresponding bidentate donor in a 1:1 stoichiometric ratio in hexane, two dimers [donor·CsHMDS]$_2$ [donor = (*R*,*R*)-TMCDA for **5** and TMEDA for **6** in 41% and 21% crystalline yields, respectively] were synthesized from respective *n*-hexane solutions (Scheme 4). These yields were not optimized, and **5** and **6** were highly soluble in *n*-hexane.

Interestingly, when an *n*-hexane/toluene mixture of solvents was used for the synthesis of **6**, the toluene solvate, **4** was isolated. This provides experimental evidence that heavier alkali metals favor softer metal-π interactions with arenes rather than dative bonding to harder amino ligands.

When the bidentate ligand is substituted for the tridentate N-donor *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) (Scheme 4), a complex with a dimeric motif similar to that of **5** and **6**, [PMDETA·CsHMDS]$_2$ **7** (68%), was obtained (Scheme 4). Compound **7** was first isolated from the reaction of [LiCs(HMDS)$_2$]$_\infty$ **2** in *n*-hexane with PMDETA in a 1:2 stoichiometric ratio. Nichols et al. reported NMR spectroscopic experiments involving a mixture of LiHMDS and KHMDS in a 1:1 stoichiometric ratio with addition of TMEDA. These results showed monomeric [TMEDA·LiHMDS] and dimeric [TMEDA·KHMDS]$_2$ species were present, interestingly with no NMR spectroscopic evidence for formation of mixed alkali metal HMDS aggregates in the presence of only TMEDA.[39]

The reaction combining the tetradentate ligand tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) and CsHMDS initially in a 1:1 ratio yielded the tetranuclear aggregate [{Me$_6$-TREN·Cs(HMDS)}$_2${Cs(HMDS)}$_2$] **8**. Similar moieties have been reported for KR compounds [R = CH(SiMe$_3$)$_2$],[40] but as far as we are aware, this is the first in Cs amide chemistry. In an attempt to optimize the reaction conditions, the stoichiometry of the reaction was adjusted to 2:1 CsHMDS:Me$_6$TREN, and **8** was isolated in a moderate crystalline yield of 50% (Scheme 4).

In our attempt to expand the scope of the reaction to smaller (and by implication more reactive) aggregates, a *n*-hexane suspension of CsHMDS was reacted with the strong chelating heptadentate tris[2-(2-methoxyethoxy)ethyl]amine (TMEEA) producing a dark brown oil. After addition of toluene, a brown solution was obtained which was stored at −33 °C to produce crystals of the monomeric species [TMEEA·CsHMDS] **9** (49%) (Scheme 4).

X-ray Diffraction Studies. Compounds **2**, **3**, and **5**–**9** were successfully prepared and characterized in the solid state by X-ray diffraction studies (full details are given in Tables S2 and S3). Crystals of **2** and **3** were obtained from cocomplexation reactions of the homometallic amides in solution, while **5**–**9** were obtained from the appropriate CsHMDS/donor solution as detailed in the Experimental Section. All the reactions were optimized for the production of high quality crystals suitable for X-ray diffraction studies.

Complexes **2** and **3** consist of an early (Li or Na, respectively) and heavy alkali metal Cs bis(trimethylsilyl)amide (HMDS) unit building polymeric assemblies. However, distinct polymeric arrays are obtained depending on the size of the lighter alkali metal cation. To the best of our knowledge, [LiCs(HMDS)$_2$]$_\infty$ **2** represents the second example of an

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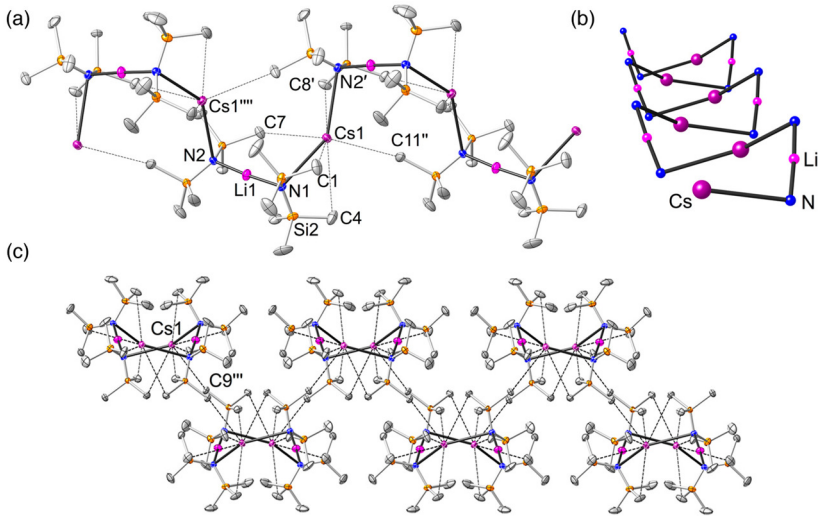

Figure 1. (a) Molecular structure of $[LiCs(HMDS)_2]_\infty$ **2** showing a section of the polymeric chain. Hydrogen atoms and one component of a disordered $SiMe_3$ groups are omitted for clarity. The displacement ellipsoids are displayed at 35% probability. (b) Ball and stick representation in perspective mode along the crystallographic *b*-axis showing the Cs−N−Li-N wave-like chain arrangement where the $SiMe_3$ groups have been omitted for clarity. (c) Section of the packing diagram showing the zigzag array between polymeric chains in the crystallographic *a*,*c*-plane. The dashed lines illustrate Cs···Me agostic interactions. Selected bond distances (Å) and angles (deg): Cs(1)−N(1) 3.289(3), Cs(1)−N(2)′ 3.345(2), Cs(1)−C(1) 3.623(4), Cs(1)−C(3)′ 3.879(5), Cs(1)−C(8)′ 3.759(4), Cs(1)−C(4) 3.761(5), Cs(1)−C(7) 3.739(4), Li(1)−N(1) 1.919(6), Li(1)−N(2) 1.921(6), Cs(1)−C(9)‴ 3.823(3); N(1)−Li(1)−N(2) 175.7(4), Li(1)−N(1)−Cs(1) 102.8(2), N(1)−Cs(1)−N(2)′ 141.30(6), Li(1)−N(2)−Cs(1)⁗ 100.9(2). The symmetry operation used to generate the equivalent atoms labeled with ′, ″, ‴ and ⁗ are $3/2 - x$, $1/2 + y$, z, x, $y + 1$, z, $1 - x$, $-y$, $-z$ and $3/2 - x$, $y - 1/2$, z, respectively.

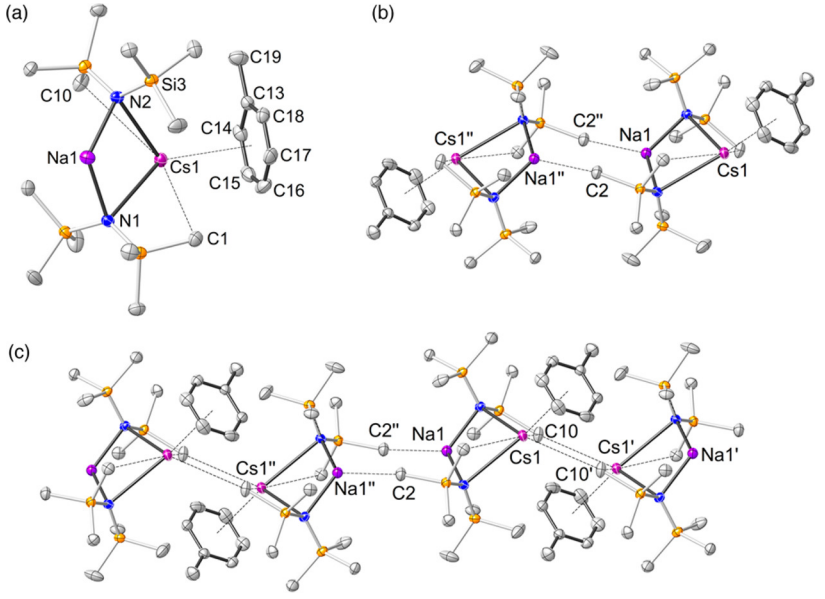

Figure 2. (a) Molecular structure of $[toluene{\cdot}NaCs(HMDS)_2]_\infty$ **3** showing the contents of the asymmetric unit which corresponds to a [toluene·$NaCs(HMDS)_2$] unit. Hydrogen atoms are omitted for simplicity and displacement ellipsoids are displayed at 35% probability. (b) Section of the polymeric chain showing the Na···Me between dimeric [toluene·$NaCs(HMDS)_2$] units. (c) Section of the polymeric chain showing the Cs···Me interactions. Selected bond distances (Å) and angles (deg): Na(1)−N(1) 2.362(3), Na(1)−N(2) 2.336(4), Cs(1)−N(1) 3.152(3), Cs(1)−N(2) 3.121(3), Cs(1)−C(1) 3.641(4), Cs(1)−C(10) 3.700(4), Na(1)−C(2)″ 2.871(4), C(2)−Na(1)″ 2.871(4), C(10)−Cs(1)′ 3.691(4), Cs(1)−C(10)′ 3.691(4); Na(1)−N(1)−Cs(1) 80.46(9), Na(1)−N(2)−Cs(1) 81.50(10), N(2)−Na(1)−N(1) 118.09(12), N(2)−Cs(1)−N(1) 79.92(8). The symmetry operation used to generate the equivalent atoms labeled with ′ and ″ are $1 - x$, $2 - y$, $2 - z$ and $-x$, $1 - y$, $1 - z$, respectively.

unsolvated lithium-containing mixed-alkali metal HMDS species; only the unsolvated $[LiK(HMDS)_2]$ is known.[41] Complex **2** adopts a wave-like polymeric chain arrangement composed of alternating $[LiCs(HMDS)_2]$ units along the crystallographic *b*-axis (Figure 1a,b). Mirroring $[LiK(HMDS)_2]$, the $[LiCs(HMDS)_2]$ units adopt a notable open [Li−N−Cs-N] array. This "open" dimeric arrangement is a distinctive structural feature when comparing with other related heteroalkali metal HMDS amides salts which normally adopt a $[M(\mu\text{-}N_2)M']$ heterodimeric ring in the presence of THF as a donor molecule.[36]

The asymmetric unit contains Cs and Li cations and two bridging HMDS anions that link the metals through the N atoms, allowing the aforementioned propagation along the

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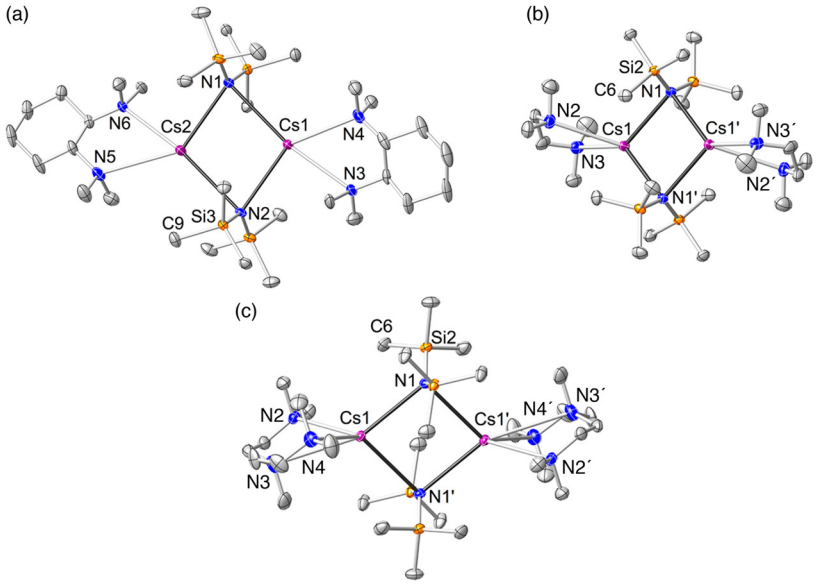

Figure 3. (a) Molecular structure of $[(R,R)\text{-TMCDA}\cdot\text{CsHMDS}]_2$ **5**, (b) $[\text{TMEDA}\cdot\text{CsHMDS}]_2$ **6** and (c) $[\text{PMDETA}\cdot\text{CsHMDS}]_2$ **7**. Hydrogen atoms, and one disordered component of the (*R*,*R*)-TMCDA, TMEDA and PMDETA ligands in **5**, **6**, and **7**, respectively, are omitted for clarity. Displacement ellipsoids are displayed at 35% probability. Selected bond distances (Å) and angles (deg) for **5**: Cs(1)−N(1) 3.310(3), Cs(1)−N(2) 3.112(3), Cs(1)−N(3) 3.172(4), Cs(2)−N(1) 3.123(3), Cs(2)−N(2) 3.325(3), Cs(2)−N(5) 3.302(4), Cs(2)−N(6) 3.242(4); Cs(1)−N(2)−Cs(2) 80.80(7), Cs(2)−N(1)−Cs(1) 80.89(8), N(3)−Cs(1)−N(4) 51.51(18), N(6)−Cs(2)−N(5) 52.02(9); for **6**: Cs(1)−N(1) 3.0551(18), Cs(1)−N(1)′ 3.1920(18), Cs(1)−N(2) 3.288(2), Cs(1)−N(3) 3.183(2), Cs(1)−C(1)′ 3.679(3); Cs(1)−N(1)−Cs(1)′ 86.26(4), N(1)−Cs(1)−N(1)′ 93.74(4), N(3)−Cs(1)−N(2) 56.41(6); and for **7**: Cs(1)−N(1) 3.2134(16), Cs(1)−N(1)′ 3.1637(17), Cs(1)−N(2) 3.3316(19), Cs(1)−N(3) 3.4229(19), Cs(1)−N(4) 3.3010(18); N(1)′−Cs(1)−N(1) 86.43(4), Cs(1)′−N(1)−Cs(1) 93.57(4); N(4)−Cs(1)−N(2) 96.37(5), N(4)−Cs(1)−N(3) 52.68(5), N(2)−Cs(1)−N(3) 53.54(5). The symmetry operation used to generate the equivalent atoms labeled with ′ in **6** and **7** are $1/2 - x, 1/2 - y, 1 - z$ and $1 - x, 1 - y, 1 - z$, respectively.

crystallographic *b* axis. While the N−Li−N angle is close to linearity [175.7(4)°], the N−Cs−N angle is narrower [141.30(6)°]. Each Li and Cs cation thus presents a formal coordination number of two with respect to N_{amido} ions. However, in addition each Cs cation exhibits seven long Cs···Me agostic-type interactions [Cs···C range 3.623(4)−3.879(5) Å] with neighboring $SiMe_3$ groups. These both help to support the growth of the chain and interconnect neighboring chains. Significant structural modifications are noted when the larger alkali metal Na is introduced in place of the Li cations. In contrast to the open chain like [Li−N−Cs-N] motif observed in **2**, the structure of $[\text{toluene}\cdot\text{NaCs(HMDS)}_2]_\infty$ **3** is comprised of solvated four-membered [Na−N−Cs−N] cyclo-dimeric units as commonly observed in other hetero bialkali metal HMDS species.[36] The HMDS ligands asymmetrically bridge Na to Cs, with Na−N bond lengths of 2.336(4) and 2.362(3) Å and Cs−N bond lengths of 3.121(3) and 3.152(3) Å. This situation leaves the larger Cs metal center coordinatively unsaturated, thus allowing the coordination of one molecule of toluene via π-arene bonding interactions [Cs··· arene(centroid), 3.339 Å] and three close Cs···Me contacts [Cs···C range 3.641(4)−3.700(4) Å]. This type of η^6-bonding of an arene is a common feature found in alkali metal organometallic complexes.[42] There are also short Na···Me contacts, and the Na···C2 contacts [2.871(4) Å] connect the $[\text{toluene}\cdot\text{NaCs(HMDS)}_2]$ units into pairs, and Cs···Me contacts then connect these dimeric Na/Cs units and so allow the growth of **3** as a polymeric chain in the solid state (Figure 2).

Compounds **5**, **6**, and **7** all crystallize in the monoclinic crystallographic system and consist of planar four-membered homometallic [Cs−N−Cs−N] (N from HMDS) cyclo-dimers with a bidentate [(*R*,*R*)-TMCDA for **5** and TMEDA **6**] or tridentate (PMDETA for **7**) N donor ligand terminally coordinated to each Cs atom (Figure 3). Two sets of shorter and longer Cs−N bond lengths are found in the Cs_2N_2 rings for **5**−**7** [short: Cs1−N2 and Cs2−N1 bond lengths of 3.112(3) and 3.123(3) Å, respectively, for **5**, Cs1−N1 of 3.0551(18) Å for **6** and Cs1−N1 of 3.1637(17) Å for **7**; long: Cs1−N1 and Cs2−N2 bond lengths of 3.310(3) and 3.325(3) Å, respectively, for **5**, Cs1−N1′ of 3.1920(18) for **6** and 3.2134(16) for **7**, Figure 3]. A similar trend is observed for the N_{donor} to the Cs metal center when the donor molecule is (*R*,*R*)-TMCDA or TMEDA for **5** and **6**, respectively [short: Cs1−N3 and Cs2−N6 bond lengths of 3.172(4) and 3.242(4) for **5**, and Cs1−N3 of 3.183(2) for **6**; long: Cs2−N5 bond length of 3.302(4) for **5**, and Cs1−N2 of 3.288(2) Å for **6**, Figure 3]. For **7**, the N_{donor}−Cs bond lengths are 3.3010(18) and 3.3316(19) Å with the two lateral N4 and N2 atoms from the PMDETA ligand, respectively, whereas it is longer with the central N3 atom [3.4229(19) Å]. This variance in the Cs−N bond lengths can be explained by the presence of $N_{anionic}$ and N_{dative} interactions with the Cs metal cations. Note that although **5** and **6** both have bidentate donor ligands, these are orientated differently with TMEDA lying approximately perpendicular to the [Cs−N−Cs−N] ring in **6** but (*R*,*R*)-TMCDA oriented roughly coplanar with [Cs−N−Cs−N] in **5**. The Cs−N_{amido}−Cs bond angles in **5**, **6**, and **7** depend on the nature of the donor ligand, which is coordinated to the Cs cation. An increase in the Cs−N−Cs angle is observed when moving from bidentate (*R*,*R*)-TMCDA and TMEDA [Cs1−N1−Cs2 and Cs1−N2−Cs2 angles of 80.89(8) and 80.80(7), respectively, for **5**; and Cs1−N1−Cs1′ angle of 86.26(4)° for **6**] to the tridentate N ligand PMDETA (mean Cs−N−Cs

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angle, 93.6° for **7**). Looking at the unsolvated congener $[CsHMDS]_2$,[19] a decrease in the Cs−N−Cs angle (mean Cs−N−Cs angle, 89.6°) is observed compared to **7**. The intermetallic Cs···Cs distance in the dimeric species **5**−**7** and $[CsHMDS]_2$ also reflects the same trend observed for the Cs−N−Cs angle [Cs···Cs distance increase in the series **5** [4.1752(3) Å] < **6** [4.2719(3) Å] < $[CsHMDS]_2$ [4.4153(3) Å][19] < **7** [4.6476(3) Å]. The solid state structure of **6** can be compared and contrasted with the previously published organocesium polymer $[TMEDA{\cdot}Cs\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$ (Figure 4).[40] This complex exhibits a polymeric structure of alternating "open dimeric" [Cs−C−Cs−C] units in contrast to the discrete dimeric $[Cs_2N_2]$ units found in **6**.

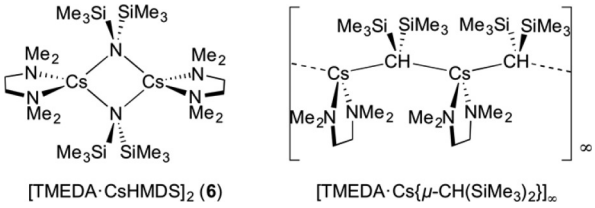

Figure 4. Structural formulas of $[TMEDA{\cdot}CsHMDS]_2$ **6** and $[TMEDA{\cdot}Cs\{\mu\text{-}CH(SiMe_3)_2\}]_\infty$.

When the bulky N tetradentate Me_6TREN donor molecule is employed, the product has two distinct Cs environments and forms $[(Me_6TREN{\cdot}CsHMDS)_2(CsHMDS)_2]$ **8** (Figure 5). Complex **8** can be considered as two dimeric [{Me_6TREN·Cs}−N−Cs−N] chains which combine, via a central planar

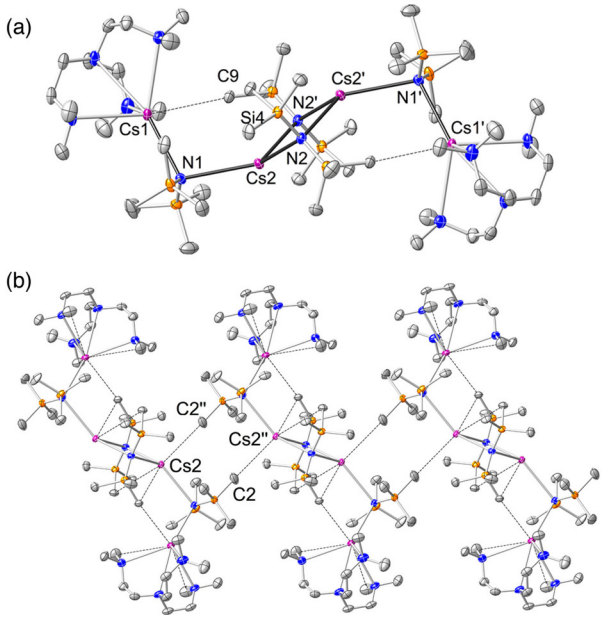

Figure 5. (a) Molecular structure of [{Me_6-TREN·Cs(HMDS)}$_2${Cs(HMDS)}$_2$] **8**. Hydrogen atoms and one disordered toluene molecule of crystallization are omitted for simplicity. Displacement ellipsoids are displayed at 35% probability. (b) Section of the polymeric arrangement showing the intermolecular Cs···Me interactions. Selected bond distances (Å) and angles (deg): Cs(1)−N(1) 3.129(2), Cs(2)−N(2) 3.149(2), Cs(2)−N(2)′ 3.168(2, Cs(2)−C(2)″ 3.687(4); Cs(1)−N(1)−Cs(2) 106.00(6), N(2)−Cs(2)−N(2)′ 92.85(5). The symmetry operation used to generate the equivalent atoms labeled with ′ and ″ are 1 − *x*, 1 − *y*, −*z* and −*x*, 1 − *y*, −*z*, respectively.

cyclo-dimer $[CsHMDS]_2$ unit. As the molecule is crystallographically centrosymmetric, the Me_6TREN units are mutually *anti* with respect to the [CsNCsN] ring plane. The Cs cations in this central dimer adopt a distorted trigonal pyramidal geometry [N2−Cs2−N2′, 92.85(5); N2−Cs2−N1, 128.29(5)°; and N2′−Cs2−N1, 125.72(5)°]. The Me_6TREN ligands coordinate to the outer Cs atoms in an η^4-fashion, rendering these five-coordinate. The three N-donor arms emerging from the central N donor in Me_6TREN are disposed in a plane whereby the cesium atom deviates by 1.69 Å. Neighboring [{Me_6-TREN·Cs(HMDS)}$_2${Cs(HMDS)}$_2$] units are linked by intermolecular Cs···Me interactions (Figure 5).

The structural motif of **8** is similar to that in the organopotassium compound $[(PMDETA{\cdot}KR)_2(KR)_2]$ complex (where R = μ-CH(SiMe$_3$)$_2$).[40] A search of the Cambridge Crystallographic Database[23b,43] reveals that **8** is the first structurally characterized example of a complex where Me_6TREN coordinates to a Cs atom.

When 1 equiv of CsHMDS reacts with stoichiometric amounts of the heptadentate N_6O ligand TMEEA, the donor ligand chelates a single Cs atom through all of its heteroatoms, stabilizing and constructing a sterically protected, discrete monomeric CsHMDS complex [TMEEA·CsHMDS] **9** (Figure 7). The coordination number of Cs is eight. Compound **9** is a rare example of a mononuclear cesium amide species, only the structure of the monometallic $[(18\text{-crown-}6){\cdot}Cs\{N(PPh_2)_2\}]$ has been previously reported.[21] Looking at the Cs−N bond lengths, two distinct distances are observed in the solid state of **9**, the shorter 3.0856(17) Å corresponds to a Cs−N σ-interaction with the amide HMDS ligand, and the longer 3.3189(15) Å corresponds to a Cs−N lone-pair dative interaction established between the Cs metal center and the N atom of the heptadentate TMEEA ligand.

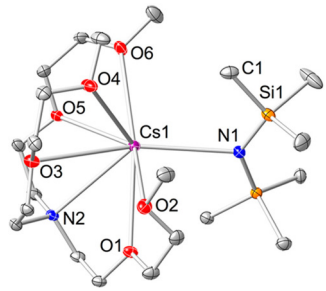

Figure 6. Molecular structure of [TMEEA·CsHMDS] **9**. Hydrogen atoms are omitted for simplicity. Displacement ellipsoids are displayed at 35% probability. Cs(1)−N(1) 3.0856(17), Cs(1)−N(2) 3.3189(15), Cs(1)−O(1) 3.1250(12), Cs(1)−O(2) 3.3554(14), Cs(1)−O(3) 3.2941(14), Cs(1)−O(4) 3.0911(13), Cs(1)−O(5) 3.1880(13), Cs(1)−O(6) 3.1520(13); N(1)−Cs(1)−N(2) 131.42(4).

NMR Spectroscopic Studies. Compounds **1**−**9** were completely characterized by ^{1}H, ^{13}C, and ^{133}Cs NMR spectroscopies in deuterated arene solvents (C_6D_6 and toluene-d_8). Resonances observed in ^{1}H and ^{13}C NMR spectra are restricted to two distinct regions, corresponding to (i) the Lewis base donor of choice; and, (ii) the HMDS group. The Lewis donor ligand/HMDS ratio found in the ^{1}H NMR spectra are 1:1 for **5**−**7** and **9**, while it is 1:2 for **8**, in agreement with the proportions expected form the solid state structures.

The ^{1}H and ^{13}C NMR spectra of compound **1** in C_6D_6 consist of a single resonance at 0.21 and 7.3 ppm, respectively, corresponding to the SiMe$_3$ group.[25c] For the heterobimetallic

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complexes **2** and **3**, singlets are observed in the ^{1}H NMR spectra in C_6D_6 at 0.27 and 0.28 ppm (6.7 and 7.3 ppm in the ^{13}C NMR spectra), respectively, which are slightly shifted downfield with respect to those of the corresponding monometallic reagents (i.e., 0.13/5.0 for LiHMDS, 0.12/6.9 for NaHMDS and 0.21/7.3 ppm for CsHMDS in the ^{1}H/^{13}C spectra). In this context, Williard et al. reported NMR spectroscopic studies which proposed the presence of a mixed-alkali metal HMDS dimeric aggregate $[(THF)_3{\cdot}LiK(HMDS)_2]_2$ in toluene-d_8 solution.[39]

In order to get more information on the aggregation states of **2** and **3** in arene solutions, a crystalline sample of each complex was treated with toluene-d_8 and studied by ^{1}H DOSY NMR spectroscopy[44] at 300 K (see Supporting Information for full details). The diffusion coefficients obtained from these studies suggest an intermediate molecular weight between the respective toluene-d_8 solvated heteroalkali metal dimeric species $[(\text{toluene-}d_8)_n{\cdot}LiCs(HMDS)_2]$ and $[(\text{toluene-}d_8)_n{\cdot}NaCs(HMDS)_2]$ and the corresponding monometallic reagents [i.e., $[(\text{toluene-}d_8)_n{\cdot}LiHMDS]_n$, $[(\text{toluene-}d_8)_n{\cdot}NaHMDS]_n$ and $[(\text{toluene-}d_8)_n{\cdot}CsHMDS]_n$] in the same solvent. This trend reflects partial deaggregation of **2** and **3** in toluene-d_8 solution producing the corresponding monometallic species, which through fast equilibria would exchange their HMDS ligands at 300 K. A variable temperature ^{1}H NMR spectroscopic study of **2** in toluene-d_8 solution shows that this dynamic equilibrium still exists at 193 K (a single resonance at 0.41 ppm is observed for the HMDS ligand at 193 K; see Supporting Information).

Focusing on the dimeric species **5**−**7**, the amido region in the ^{1}H NMR spectra obtained from C_6D_6 solutions at 300 K consist of a single resonance corresponding to the $SiMe_3$ group (0.25, 0.23, and 0.27 ppm for **5**−**7**, respectively) which appears close to that of free CsHMDS in the same solvent (0.21 ppm). Looking at the Lewis donor ligand region in each ^{1}H and ^{13}C spectra, the chemical shifts of the resonances are close to that of the corresponding noncoordinated donor molecules in the same solvent (Table S1). In agreement with these results, a ^{1}H DOSY NMR spectroscopic study of **6** (as a case of study) in toluene-d_8 at 300 K shows distinct values for the diffusion coefficients corresponding to HMDS and TMEDA ligands (9.583×10^{-10} and 1.805×10^{-9} m^2 s^{-1}, respectively), which in addition are distinct from those expected for **6**, and for the values of CsHMDS or TMEDA in toluene-d_8 solutions (8.764×10^{-10} for CsHMDS and 2.00×10^{-9} m^2 s^{-1} for TMEDA, Figure S43). This data would indicate that a fast coordination/decoordination process involving TMEDA and toluene-d_8 molecules is operating in toluene-d_8 solutions of **6** at 300 K. Fast exchange equilibria comprising different Lewis donor and arene molecules have been previously observed in arene solutions of other alkali metal amide species [i.e., $[\text{TMEDA}{\cdot}Li_2K(DA)_3]$ and $[\text{THF}{\cdot}Li(TMP)]_2$].[45,46]

Complex **6** in toluene-d_8 solution was studied by ^{1}H VT NMR spectroscopy (Figure 7). As alluded to earlier, the ^{1}H NMR spectrum of a toluene-d_8 solution of **6** at 300 K suggests that the TMEDA ligand is not bound to the cesium metal amide. However, as the temperature is decreased to 203 K, the data suggest that the "donor" TMEDA molecule does bind to the cesium metal complex. In addition, the ^{133}Cs NMR spectrum of **6** in toluene-d_8 solution is similar to that of CsHMDS in the same solvent at 300 K (126.8 vs 123.0 ppm, respectively), and it is shifted as the temperature decreased to 203 K (156.1 ppm; see Supporting Information).

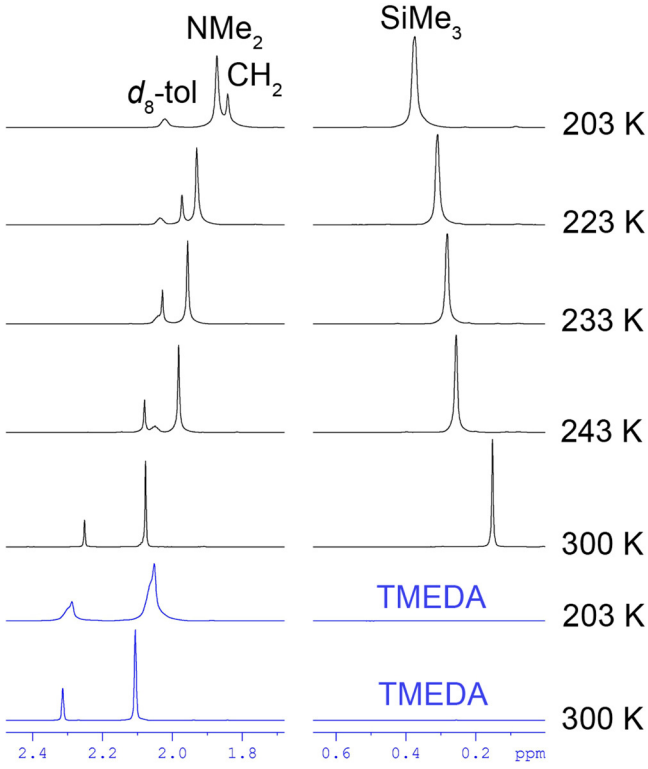

Figure 7. Variable temperature ^{1}H NMR study of a solution of **6** in toluene-d_8 from 300 to 203 K, showing coordination of TMEDA binding to CsHMDS at 203 K. ^{1}H NMR spectra of uncoordinated TMEDA at 300 and 203 K are shown in blue.

To show that this is a genuine effect caused by the cesium metal species, a ^{1}H VT NMR spectroscopic study of a sample of TMEDA in toluene-d_8 was also carried out. The data show that the chemical shifts of the free bidentate ligand are not altered in this experiment in comparison with the ^{1}H VT NMR spectroscopic study of **6** in the same solvent (Figure 7). In addition, the 1:1 CsHMDS/TMEDA ratio is maintained for **6** in toluene-d_8 solution at the variety of temperatures studied (in the range 300−203 K).

Turning to **8**, only a single ^{1}H NMR HMDS resonance at 0.24 (and ^{13}C NMR at 7.4 ppm) is observed in C_6D_6 solution at 300 K, contrasting with the presence of two distinct HMDS ligands within the solid state structure of **8**. In addition, the resonances for the tetra-dentate Me_6TREN ligand in **8** are close to that of free Me_6TREN in the ^{1}H NMR spectrum in C_6D_6 at 300 K [Me_6TREN in **8**: 2.09 (Me), 2.29 (β-CH_2) and 2.53 ppm (α-CH_2); free Me_6TREN: 2.12 (Me), 2.37 (β-CH_2), and 2.63 ppm (α-CH_2)]. In keeping with **6**, these data suggest deaggregation of dimeric tetranuclear **8** in C_6D_6 solution at 300 K. To ascertain the aggregation state of **8** in arene solutions, a crystalline sample of **8** was treated with toluene-d_8 and a ^{1}H DOSY NMR spectroscopic study was carried out at 300 K. The distinct diffusion coefficients observed for the HMDS and Me_6TREN ligands (9.038×10^{-10} and 1.0148×10^{-9} m^2 s^{-1}, respectively) indicate partial decoordination of the "donor" Me_6TREN ligand from the cesium metal amide, thus suggesting the presence of a competition process between toluene-d_8 and Me_6TREN molecules to coordinate the cesium cation.

In the monomeric complex **9**, a single resonance at 0.51 ppm is observed in the ^{1}H NMR spectrum in C_6D_6 solution at 300 K for the $SiMe_3$ group (7.6 ppm in the ^{13}C NMR spectrum). The

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chemical shifts for the resonances of the heptadentate TMEEA ligand in **9** are different to those of the free Lewis base ligand both in the ^{1}H and ^{13}C NMR spectra in the same conditions (see Table S1). To further study the aggregation state of **9** (to determine whether the TMEEA ligand is coordinated to the cesium HMDS reagent in **9** in arene solutions), a ^{1}H DOSY NMR study was carried out in toluene-d_8 at 300 K. The coefficient diffusion values obtained indicate the presence of a species with an intermediate molecular weight between [TMEEA·CsHMDS] **9** and [(toluene-d_8)$_n$·CsHMDS] (see Supporting Information for full details). Mirroring the solution behavior observed for **6** and **8** in the same conditions, this result is in agreement with the presence of a dynamic process involving the competition between the TMEEA ligand and toluene-d_8 molecules to coordinate the cesium cation in toluene-d_8 solution at 300 K.

CONCLUSIONS

By combining commercially available/easily prepared LiHMDS with CsF, the cesium amide CsHMDS has been prepared in a facile manner, which negates the use of pyrophoric cesium metal. The CsHMDS can then be utilized as a reagent by combining it with lighter alkali metal (Li or Na) HMDS complexes to cocomplex the two reagents to produce polymeric mixed alkali metal amide species. In addition, by judicious choice of donor ligand, it has been shown that CsHMDS can display a variety of oligomerization states—closed dimeric [with (*R*,*R*)-TMCDA, TMEDA, or PMDETA], tetranuclear open dimeric (with Me_6-TREN), and a rare example of a monomeric cesium amide (with TMEEA). Given the current interest in CsHMDS in synthetic organic chemistry, and indeed the use of heavier alkali metal amides in super basic mixtures, future studies will assess the reactivity of these reagents in this area.

EXPERIMENTAL SECTION

Crystallographic Analysis. Crystallographic data were recorded on Oxford Diffraction Xcalibur and Gemini diffractometers with Cu−Kα radiation (λ = 1.5418 Å) for **2** and **3** and Mo−Kα radiation (λ = 0.71073 Å) for the other structures. Measurements were made at 123(2) K except for **6** where measurements were made at 150(2) K. Structures were refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL-2013.[47] The geometries of the disordered groups were restrained to approximate typical values. An analytical absorption correction was applied in **3** using a multifaceted crystal model[48] and spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm (CrysAlisPro, Oxford Diffraction Ltd.). Selected crystallographic parameters are given in Tables S2 and S3 and full details are given in the deposited cif files (CCDC 1447680−1447686 for **2**, **3**, and **5**−**9**, respectively). These data in cif format can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

General Procedures. All reactions were performed under argon atmosphere using standard Schlenk techniques. *n*-Hexane, toluene, and tetrahydrofuran (THF) were distilled under reflux with sodium metal and benzophenone within a nitrogen atmosphere. C_6D_6 was degassed and stored under argon over activated molecular sieves (4 Å) prior to use. Bis(trimethylsilyl)amine [HMDS(H)], *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich, distilled under nitrogen atmosphere with CaH_2, and stored under argon over activated molecular sieves (4 Å). Tris{2-(dimethylamino)-ethyl}amine (Me_6TREN) and (*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA] were prepared according to literature methods, and stored under argon over activated molecular sieves (4 Å). Tris{2-(2-methoxyethoxy)ethyl}amine (TMEEA) was purchased from Aldrich and used as received. CsF was purchased from Aldrich and dried under vacuum at 150 °C for 5 days and stored in a glovebox. LiHMDS was prepared reacting *n*-BuLi and HMDS(H) according to literature methods and stored in a glovebox. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.1, 100.6, and 52.5 for ^{1}H, ^{13}C and ^{133}Cs, respectively. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts are expressed in parts per million (ppm) and referenced to residual solvent peaks. ^{133}Cs NMR spectra were referenced against an external standard solution of CsF (1 M in D_2O, δ = 0 ppm). Microanalysis was obtained for all compounds using a PerkinElmer 2400 elemental analyzer.

*Synthesis of CsHMDS (**1**).* A 1.6 M solution of *n*-BuLi in hexanes (18.75 mL, 30 mmol) was added dropwise to a solution of HMDS(H) (6.3 mL, 30 mmol) in *n*-hexane (40 mL) and the reaction was stirred for 2 h. CsF (4.56 mg, 30 mmol) was added using a solid addition tube, and the reaction mixture was refluxed for 15 h at 68 °C to yield a pale gray suspension. The reaction was cooled to ambient temperature, the solvent removed under a vacuum, and toluene (60 mL) was added. The reaction was filtered and the solid washed with toluene (2 × 15 mL). The solvent of the colorless solution was removed under a vacuum and the resultant white product was sublimed (200 °C, 5 h) to yield white crystals of **1**. Yield: 7 g, 23.87 mmol, 80%. ^{1}H NMR (400.01 MHz, 300 K, C_6D_6): δ 0.21 (s, 18 H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, 300 K, C_6D_6): δ 7.3. ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 119.2 (s). Anal. Calcd (Found) for $C_6H_{18}CsNSi_2$: C, 24.57 (24.61); H, 6.19 (6.19); N, 4.78% (4.91%).

*Synthesis of [LiCs(HMDS)$_2$]$_\infty$ (**2**).* LiHMDS (670 mg, 4 mmol) was suspended in *n*-hexane (20 mL) and cesium fluoride (304 mg, 2 mmol) added using a solid addition tube. The reaction was refluxed for 8 h at 68 °C, and the solvent was evacuated to dryness. Toluene (10 mL) was added and the reaction was heated and filtered obtaining a colorless solution. Crystals of **2** suitable for X-ray study crystallized at −33 °C from a *n*-hexane/toluene (7/5 mL) mixture after 24 h. Compound **2** was filtered, washed with *n*-hexane (10 mL) and dried under a vacuum for 10 min. Yield (based on the consumption of CsF): 520 mg, 1.13 mmol, 57%. ^{1}H NMR (400.01 MHz, 300 K, C_6D_6): δ 0.27 (s, 36 H). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, 300 K, C_6D_6): δ 6.7. ^{7}Li NMR (155.47 MHz, 300 K, C_6D_6): δ 1.8. ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 54.2 (v br s). Anal. Calcd (Found) for $C_{12}H_{36}CsLiN_2Si_4$: C, 31.29 (32.02); H, 7.88 (8.02); N, 6.08% (6.04%).

*Synthesis of [toluene·NaCs(HMDS)$_2$]$_\infty$ (**3**).* NaHMDS (184 mg, 1 mmol) and CsHMDS (293 mg, 1 mmol) were suspended in *n*-hexane (10 mL), and the reaction mixture was stirred for 5 min. Toluene (2 mL) was added to obtain a colorless solution and the reaction was stored at −33 °C where **3** crystallized as colorless crystals suitable for an X-ray diffraction study after 24 h. **3** was filtered, washed with *n*-hexane (10 mL), and dried under a vacuum for 3 min. Yield: 350 mg, 0.62 mmol, 62%. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.18 (s, 36 H, Me_3Si), 2.11 (s, 3 H, *Me*-toluene), 7.02 (m, 3 H, *ortho* + *para*-*CH*), 7.13 (m, 2 H, *meta*-*CH*). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ 7.3 (Me_3Si), 21.5 (*Me*-toluene), 125.7 (*para*-CH), 128.6 (*meta*-CH), 129.3 (*ortho*-CH), 137.9 (C-toluene). ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 92.0 (v br s). Anal. Calcd (Found) for $C_{12}H_{36}CsN_2NaSi_4$: C, 30.24 (29.90); H, 7.61 (7.52); N, 5.88% (5.69%).

*Synthesis of [(R,R)-TMCDA·CsHMDS]$_2$ (**5**).* CsHMDS (293 mg, 1 mmol) was suspended in *n*-hexane (10 mL), and the reaction mixture was stirred for 10 min. After that, (*R*,*R*)-TMCDA (0.19 mL, 1 mmol) was added to yield a colorless solution. The reaction was filtered via cannula, and the solution was stored at −33 °C where **5** crystallized as colorless crystals suitable for an X-ray diffraction study after 24 h. Compound **5** was filtered, washed with *n*-hexane (10 mL), and dried under a vacuum for 5 min. Yield: 190 mg, 0.21 mmol, 41%. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.25 (s, 18 H, Me_3Si), 0.97 (s, 4 H, β/γ CH_2-(*R*,*R*)-TMCDA), 1.58 (s, 2 H, β/γ-CH_2-(*R*,*R*)-TMCDA), 1.72 (s, 2 H, β/γ-CH_2-(*R*,*R*)-TMCDA), 2.2 (s, 2 H, α-CH-(*R*,*R*)-TMCDA), 2.23 (s, 12 H, Me-(*R*,*R*)-TMCDA). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ 7.4 (Me_3Si), 25.1 (β-CH_2-(*R*,*R*)-TMCDA), 25.9 (γ-CH_2-(*R*,*R*)-TMCDA), 40.5 (*Me*-(*R*,*R*)-TMCDA),

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64.3 (α-CH-(*R*,*R*)-TMCDA). ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 123.19 (br s). Anal. Calcd (Found) for $C_{32}H_{80}Cs_2N_6Si_4$: C, 41.45 (41.46); H, 8.70 (8.64); N, 9.06% (9.35%).

*Synthesis of [TMEDA·CsHMDS]$_2$ (**6**).* CsHMDS (587 mg, 2 mmol) was suspended in *n*-hexane (10 mL), and the reaction mixture was stirred for 10 min. After that, TMEDA (0.3 mL, 2 mmol) was added to yield a colorless solution. The reaction was filtered via cannula, concentrated (5 mL), and stored at −33 °C where **6** crystallized as colorless crystals suitable for an X-ray diffraction study after 24 h. Compound **6** was filtered, washed with *n*-hexane (10 mL), and dried under a vacuum for 5 min. Yield: 170 mg, 0.21 mmol, 21%. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.23 (s, 36 H, Me_3Si), 2.08 (s, 24 H, CH_3-TMEDA), 2.28 (s, 8 H, CH_2-TMEDA). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 7.3 (Me_3Si), 45.9 (CH_3-TMEDA), 58.2 (CH_2-TMEDA). ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 126.2 (s). According to ^{1}H NMR there is a deficit of ligand molecules with respect to CsHMDS (1.61 molecules of TMEDA vs 2 molecules of TMEDA found in solid state) due to evacuation of some molecules of the ligand while drying **6**. Anal. Calcd (Found) for $C_{21.78}H_{62.08}Cs_2N_{5.26}Si_4$: C, 33.71 (33.56); H, 8.06 (7.82); N, 9.49% (9.28%).

*Synthesis of [PMDETA·CsHMDS]$_2$ (**7**).* CsHMDS (587 mg, 2 mmol) was suspended in *n*-hexane (10 mL), and the reaction mixture was stirred for 10 min. After that, PMDETA (0.42 mL, 2 mmol) was added, and the reaction heated with a hot gun and placed inside a hot water bath where **7** crystallized as colorless crystals suitable for an X-ray after 24 h. **7** was filtered, washed with *n*-hexane (15 mL) and dried under a vacuum for 5 min. Yield: 620 mg, 0.68 mmol, 68%. ^{1}H NMR (400.1 MHz, 300 K, C_6D_6): δ 0.27 (s, 18 H, $SiCH_3$), 2.09 (s, 12 H, Me_2N-PMDETA), 2.12 (s, 3 H, *Me*N-PMDETA), 2.25 (m, 4H, CH_2-PMDETA), 2.34 (m, 4H, CH_2-PMDETA). ^{13}C{^{1}H} NMR (100.6 MHz, 300 K, C_6D_6): δ 7.4 ($SiCH_3$), 42.8 (*Me*N-PMDETA), 45.8 (Me_2N-PMDETA), 56.7 (CH_2-PMDETA), 58.0 (CH_2-PMDETA). ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 129.7 (s). Anal. Calcd (Found) for $C_{30}H_{82}Cs_2N_8Si_4$: C, 38.61 (38.79); H, 8.86 (9.04); N, 12.01% (12.14%).

*Synthesis of [(Me_6TREN·CsHMDS)$_2$(CsHMDS)$_2$] (**8**).* CsHMDS (587 mg, 2 mmol) was suspended in *n*-hexane (10 mL), and the reaction mixture was stirred for 10 min. Me_6TREN (0.27 mL, 1 mmol) was added, and the reaction was stirred for 10 min to yield an orange suspension. Crystals of **8** suitable for an X-ray diffraction study grow from a mixture of *n*-hexane/toluene (5/8 mL) at −33 °C after 1 month. Compound **8** was filtered, washed with *n*-hexane (3 × 3 mL) and dried under a vacuum for 5 min. Yield: 410 mg, 0.25 mmol, 50%. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.24 (s, 36 H, Me_3Si), 2.09 (s, 18 H, Me-Me_6TREN), 2.29 (t, 6 H, $^3J_{HH}$ = 6.7 Hz, α/β-CH_2-Me_6TREN), 2.53 (t, 6 H, $^3J_{HH}$ = 5.07 Hz, α/β-CH_2-Me_6TREN). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 7.4 (Me_3Si), 45.9 (*Me*-Me_6TREN), 53.3 (α/β-CH_2-Me_6TREN), 58.2 (α/β-CH_2-Me_6TREN). ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 124.56 (br s). According to ^{1}H NMR there are 0.54 molecules of toluene per complex. Anal. Calcd (Found) for $C_{51.78}H_{136.32}Cs_4N_{12}Si_8$: C, 36.94 (37.55); H, 8.16 (8.00); N, 9.98% (10.09%).

*Synthesis of [TMEEA·Cs(HMDS)] (**9**).* CsHMDS (587 mg, 2 mmol) was suspended in *n*-hexane (10 mL), and the reaction mixture was stirred for 10 min. TMEEA (0.64 mL, 2 mmol) was added, and the reaction was stirred for 10 min to yield a brown oily material. Crystals of **9** crystallized from a hexane/toluene (6/5 mL) mixture at −33 °C after 3 days. Compound **9** was filtered, washed with *n*-hexane (15 mL), and dried under a vacuum for 5 min. Yield: 600 mg, 0.97 mmol, 49%. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.51 (s, 18 H, Me_3Si), 2.30 (t, 6 H, $^3J_{HH}$ = 5.07 Hz, CH_2N-donor), 3.15 (t, 6 H, $^3J_{HH}$ = 5.07 Hz, CH_2-donor), 3.21 (s, 9 H, CH_3-donor), 3.26 (m, 6 H, CH_2-donor), 3.28 (m, 6 H, CH_2-donor). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, 300 K): δ 7.6 (Me_3Si), 55.5 (CH_2N-donor), 58.7 (CH_3-donor), 69.0 (CH_2-donor), 70.4 (CH_2-donor), 72.0 (CH_2-donor). ^{133}Cs NMR (52.5 MHz, C_6D_6, 300 K): δ 104.0 (s). Anal. Calcd (Found) for $C_{21}H_{51}CsN_2O_6Si_2$: C, 40.90 (41.11); H, 8.34 (8.24); N, 4.54% (4.70%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00839.

^{1}H, ^{133}Cs, and ^{13}C{^{1}H} NMR spectra for complexes **1**−**9** (PDF)

Crystallographic data for complexes **2**, **3**, and **5**−**9** (CIF)

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Notes

The authors declare no competing financial interest.

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