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Synthetic and Structural Studies of Mixed Sodium Bis(trimethylsilyl)amide/Sodium Halide Aggregates in the Presence of η^2-*N,N*-, η^3-*N,N,N*/*N,O,N*-, and η^4-*N,N,N,N*-Donor Ligands

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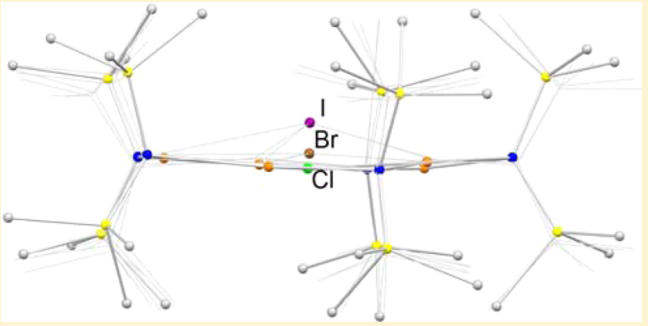
Supporting Information

ABSTRACT: When *n*-hexane solutions of an excess of sodium bis(trimethylsilyl)amide (NaHMDS) are combined with cesium halide (halide = Cl, Br, or I) in the presence of the tetradentate donor molecule [tris[2-(dimethylamino)ethyl]-amine] (Me_6TREN), the isolation and characterization of a series of sodium amide/sodium halide mixed aggregates was forthcoming. Cesium halide was employed because it efficiently reacted with NaHMDS to produce a molecular, soluble source of sodium halide salt (which was subsequently captured by an excess of NaHMDS) via a methathetical reaction. These mixed sodium amide/sodium halide complexes are formally sodium sodiates, are deficient in halide with respect to the amide, and have the general formula $[\{Na_5(\mu\text{-HMDS})_5(\mu_5\text{-X})\}\{Na(Me_6TREN)\}]$ [where X = Cl (**1**), Br (**2**), or I (**3**)]. The influence of the donor ligand was studied for the NaI/NaHMDS system, and when *n*-hexane solutions of this composition were treated with tridentate donors such as *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) or *N,N,N′,N′*-tetramethyldiaminoethyl ether (TMDAE), solvent-separated ion-pair cocomplexes $[Na_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[Na_3(\mu\text{-HMDS})_2(PMDETA)_2]^+$ (**4**) and $[Na_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[Na(TMDAE)_2]^+$ (**5**) were isolated. However, upon reaction with bidentate proligands such as the chiral diamine (*R,R*)-*N,N,N′,N′*-tetramethylcyclohexane-1,2-diamine [(*R,R*)-TMCDA] or *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), neutral complexes $[Na_4(\mu\text{-HMDS})_3(\mu_4\text{-I})(donor)_2]$ [donor = (*R,R*)-TMCDA (**6**) and TMEDA (**7**)] were produced. To illustrate the generality of the latter reaction with other halides, $[Na_4(\mu\text{-HMDS})_3(\mu_4\text{-Br})(TMEDA)_2]$ (**8**) was also prepared by employing NaBr in the synthesis instead of NaI.



INTRODUCTION

In recent years, the chemistry of alkali-metal halide salts has been the subject of intense interest in terms of their utilization in synthesis to gain a better understanding of both their modus operandi and their structures. For instance, in 2013, two high-profile reports discussed the role of alkali metals behaving more like p-block rather than s-block metals in halide salts, culminating in the theoretical prediction and experimental synthesis of unexpected species such as $NaCl_n$ and $CsCl_n$ (where $n > 1$).[1] From a synthetic standpoint, the majority of interest has been focused on the role played by LiCl. It has been shown that the presence of this salt can play a beneficial or detrimental role in the reactivity and/or selectivity of organic transformations compared with strictly salt-free (or assumed to be salt-free) protocols.[2] In this context, Knochel et al. have comprehensively studied the favorable effect that using stoichiometric quantities of LiCl in combination with a conventional Grignard (RMgX, where R = alkyl or aryl and X = halide) or Hauser (R_2NMgX, where R = alkyl and X = halide) reagent has to produce the respective so-called *turbo* reagents. These reagents enhance the reactivity/selectivity of a multitude of metal−halogen or metal−hydrogen exchange reactions.[3] Collum et al. have provided important structural insight into the solution state of secondary lithium amide bases in the presence of lithium halide salts, illustrating the superior reactivity and stereoselectivity that the utility of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) exhibits in the *E*-enolization of ketones[4] and the catalytic activity that LiCl plays in the 1,4-nucleophilic addition of lithium diisopropylamide (LDA) to unsaturated esters[5] and in the ortho metalation of arene systems containing halogen-based directing groups.[2b]

The reactivity of lithium amide reagents is highly dependent on their aggregation states. In this context, the solution[6] and solid-state structures[7] of salts of sterically demanding secondary amides have been well established. For example, LDA, which has been characterized as a helical polymer in the solid state,[7g] presents diverse cyclic polymorphs in arene solutions, with the major species being tetrameric and trimeric, but also pentamers and hexamers have been shown to exist.[6d] LiTMP exists as a cyclic trimer and tetramer in the solid state and in hydrocarbon solution,[7d,j] and lithium 1,1,1,3,3,3-hexamethyldisilazide (LiHMDS) exists as an equilibrium between dimeric and tetrameric species in hydrocarbon solvents.[6b] Although it is

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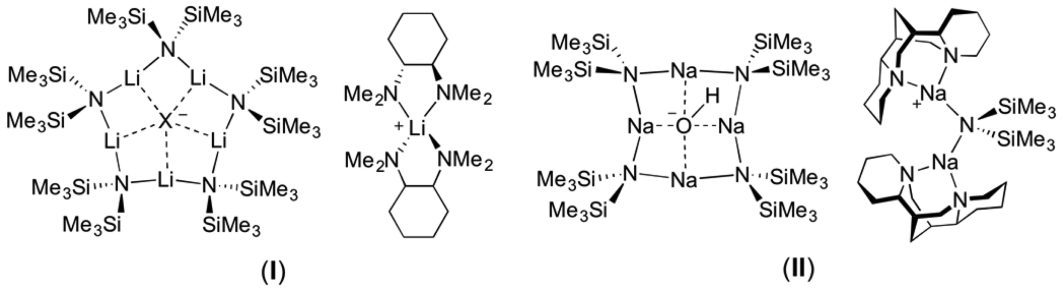
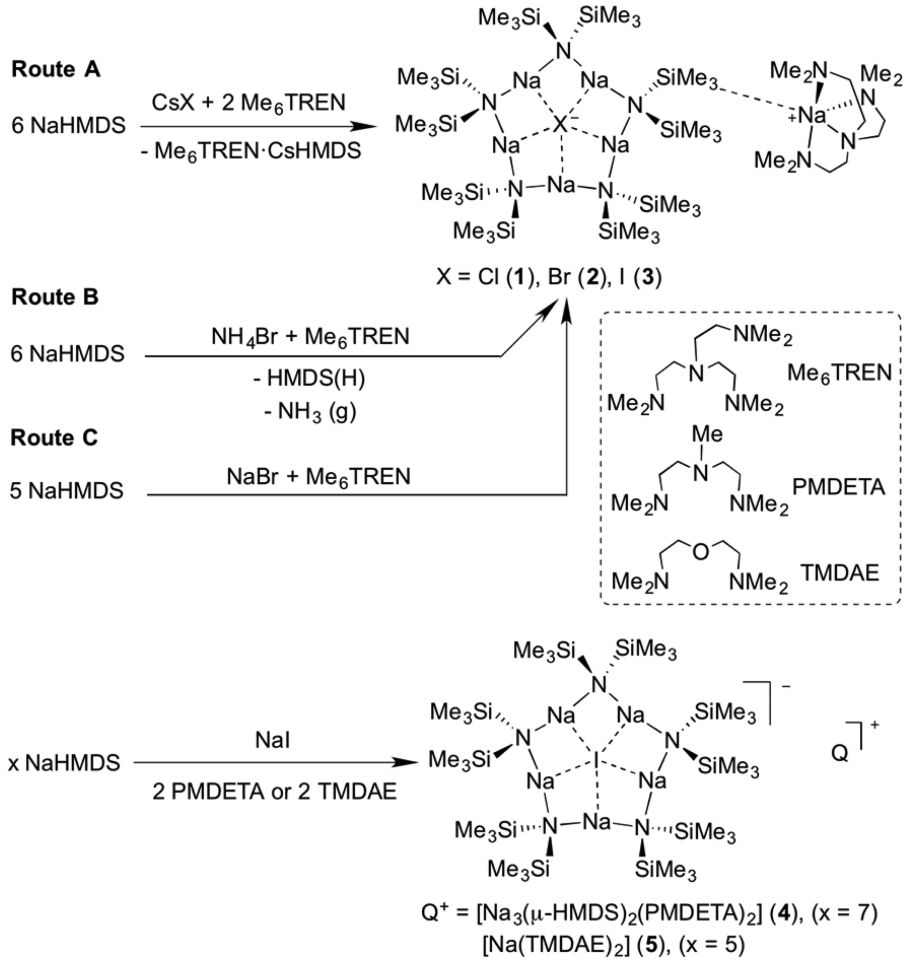


Figure 1. Structures of solvent-separated metal anionic crown complexes containing halide (**I**) and hydroxide (**II**) ions.

Scheme 1. Synthesis of 1−3 (top), and 4 and 5 (bottom)[a]



[a]Ammonium halide (route B) and sodium halide (route C) methodologies were used for the synthesis of **2**.

well-known that lithium amide reagents coordinate to lithium halides, supporting solid-state characterization of such aggregates is relatively scarce despite the numerous studies devoted to this chemistry over the past 40 or so years.[8]

We have recently shown that LiHMDS can efficiently trap substoichiometric amounts of lithium halides to form macrocyclic LiHMDS-rich complexes $[Li_5(\mu\text{-HMDS})_5(\mu_5\text{-X})]^-[Li\{(R,R)\text{-TMCDA}\}_2]^+$ [**I**, where X = Cl and Br and (*R*,*R*)-TMCDA = (*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine; Figure 1]. These solvent-separated (i.e., complexes that contain distinct anionic/cationic entities) LiHMDS/LiX aggregates have been coined metal anionic crown complexes.[8e] In contrast, the structural chemistry of sodium congeners of lithium anionic crowns and indeed other sodium amide/halide cocomplexes appears to have been neglected. A complex relevant to this particular study is the macrocyclic hydroxyl-incorporated sodium bis(trimethylsilyl)amide (NaHMDS) complex $[Na_4(\mu\text{-HMDS})_4(\mu_4\text{-OH})]^-[Na_2(\mu\text{-HMDS})\{(-)\text{-sparteine}\}_2]^+$ (**II**; Figure 1).[9] This complex can be considered as arising from the serendipitous trapping of an equivalent of "NaOH", with the OH^- being trapped within a tetrameric ring of $[Na(HMDS)]_4$ and the Na^+ cation coordinated by 2 equiv of the chiral amine (−)-sparteine.

In this study, the structural chemistry of different aggregates of the important utility amide NaHMDS[10] with several sodium halide salts in the presence of diverse Lewis donor molecules is reported. This provides further important structural insight into the way that alkali-metal amide reagents can interact with

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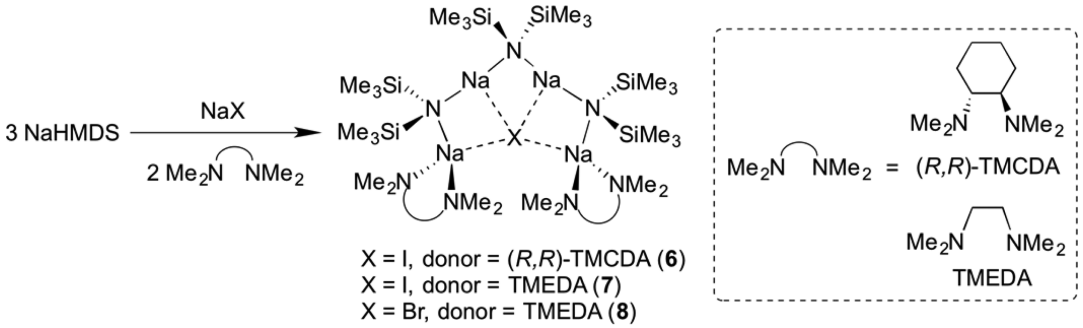
Scheme 2. Synthesis of 6−8



substoichiometric quantities of alkali-metal halide salts, a common composition encountered in certain fundamental organic transformations.[2b,5]

RESULTS AND DISCUSSION

Synthesis. The main objective of this work was to accrue structural information on the halide salt capturing ability of NaHMDS complexes. Because the primary goal was solid-state characterization, the reactions were optimized for crystallization of samples of high enough quality for X-ray crystallographic characterization. In addition, microelemental analyses in combination with NMR spectroscopy were used to determine the purity of the bulk samples and to shed light on the solution-state structures of the isolated samples.

Initially we tried to extend the work to heterobimetallic complexes by using a 6:1:2 stoichiometric mixture of NaHMDS, CsCl, and the Lewis base tris[2-(dimethylamino)-ethyl]amine (Me_6TREN). Cesium halide was chosen (rather than, for example, LiCl) because cesium is considerably larger than sodium, potentially allowing us to combat the issue of mutual substitution disorder, which commonly occurs when lithium and sodium are both present within a structure.[11] However, this synthetic route led to the preparation of an all-sodium contacted ion-pair complex, $[\{Na_5(\mu\text{-HMDS})_5(\mu_5\text{-Cl})\}\{Na(Me_6TREN)\}]$ (**1**), in moderate yield (39%). Note that all yields reported in this work (i.e., for the syntheses of **1**−**8**) are based on the consumption of alkali-metal halide. Although we did not obtain the desired heterobimetallic species, this experiment showed that CsCl appears to be an ideal source of the hydrocarbon-soluble molecular variant of *sodium chloride*, which is formed via metathesis with NaHMDS. NaCl appears to be trapped by the dual-component NaHMDS/Me_6TREN trapping system (Scheme 1). The (Me_6TREN)Cs(HMDS)-containing byproduct[12] is highly soluble in toluene, allowing the facile isolation of crystalline **1**. Complex **1** is a rare example of sodium sodiate.[9]

Because of the success of this reaction, we decided to explore its generality. The same synthetic methodology was applied to CsBr, and again a sodium-only contacted ion pair, $[\{Na_5(\mu\text{-HMDS})_5(\mu_5\text{-Br})\}\{Na(Me_6TREN)\}]$ (**2**), was formed in moderate yield (**2**, 39%; Scheme 1, route A). To assess whether it was possible to form **2** using an alternative method, ammonium halide NH_4Br and NaBr were employed as alkali-metal halide sources (Scheme 1). Complex **2** was indeed isolated albeit in lower yields (18 and 10%, respectively), suggesting that the salt metathesis reaction of NaHMDS with CsBr (Scheme 1) is a more convenient and efficient synthetic methodology to form **2**. NaI, generated in situ by the reaction of NaHMDS with CsI, was also efficiently trapped, forming a complex similar to those of **1** and **2**, $[\{Na_5(\mu\text{-HMDS})_5(\mu_5\text{-I})\}\{Na(Me_6TREN)\}]$ (**3**), in 35% yield.

With the aim of providing additional structural insight into iodide-trapped species, Me_6TREN was replaced by the tridentate amine *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA). The reaction combined NaHMDS, NaI, and PMDETA initially in a 5:1:2 stoichiometric ratio to produce $[Na_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[Na_3(\mu\text{-HMDS})_2(PMDETA)_2]^+$ (**4**). The stoichiometry of the reaction was adjusted to 7:1:2 to produce **4** in a moderate yield of 35% (Scheme 1). When *N*,*N*,*N*′,*N*′-tetramethyldiaminoethyl ether (TMDAE) was used as the donor, $[Na_5(\mu\text{-HMDS})_5(\mu_5\text{-I})]^-[Na(TMDAE)_2]^+$ (**5**) was isolated in a similar yield (36%; Scheme 1b).

Following our success in the preparation of tetra- and tridentate donor ligands containing NaHMDS/NaI cocomplexes, our work was extended to study the influence of the bidentate Lewis base donors on formation of the complexes. The donors of choice were (*R*,*R*)-TMCDA and TMEDA. By combining NaHMDS, NaI, and the corresponding bidentate donor in a 3:1:2 stoichiometrically precise ratio, two essentially isostructural compounds, $[Na_4(\mu\text{-HMDS})_3(\mu_4\text{-I})(donor)_2]$ [donor = (*R*,*R*)-TMCDA for **6** (32%) and TMEDA for **7** (44%), respectively], were formed (Scheme 2). Interestingly, through utilization of a different stoichiometric ratio of NaHMDS, NaI, and donor (5:1:2) in *n*-hexane, the same complexes were isolated. Therefore, it appears that an excess of NaHMDS (which was present for the syntheses of **1**−**5**) does not affect the preparation of **6** and **7**. To get information about the size of the halides this type of structure could accommodate, NaBr was used as the alkali-metal halide reagent in the presence of the bidentate ligand TMEDA, with NaHMDS introduced in the final step of the reaction. A complex having the same motif as **7** was obtained from this reaction in moderate yield (55%), namely, $[Na_4(\mu\text{-HMDS})_3(\mu_4\text{-Br})(TMEDA)_2]$ (**8**; Scheme 2).

X-ray Diffraction Studies. During the course of this study, seven complexes (**1**, **2**, and **4**−**8**) were successfully prepared and characterized in the solid state (full details are given in Tables S1 and S2). X-ray-quality crystals of **1**, **2**, and **4**−**8** were obtained from relevant NaHMDS/NaX solutions specified in the Experimental Section. Unfortunately, several attempts to determine the solid-state structure of **3** were unsuccessful. The X-ray data obtained for **3** was of poor quality, impeding any discussion of the structural parameters, but its chemical identity was unequivocally established as **3**.

Our X-ray diffraction studies successfully revealed structural models for species that are potentially present in solutions containing commonly employed NaHMDS and a N-donor ligand in combination with sodium halide salts.

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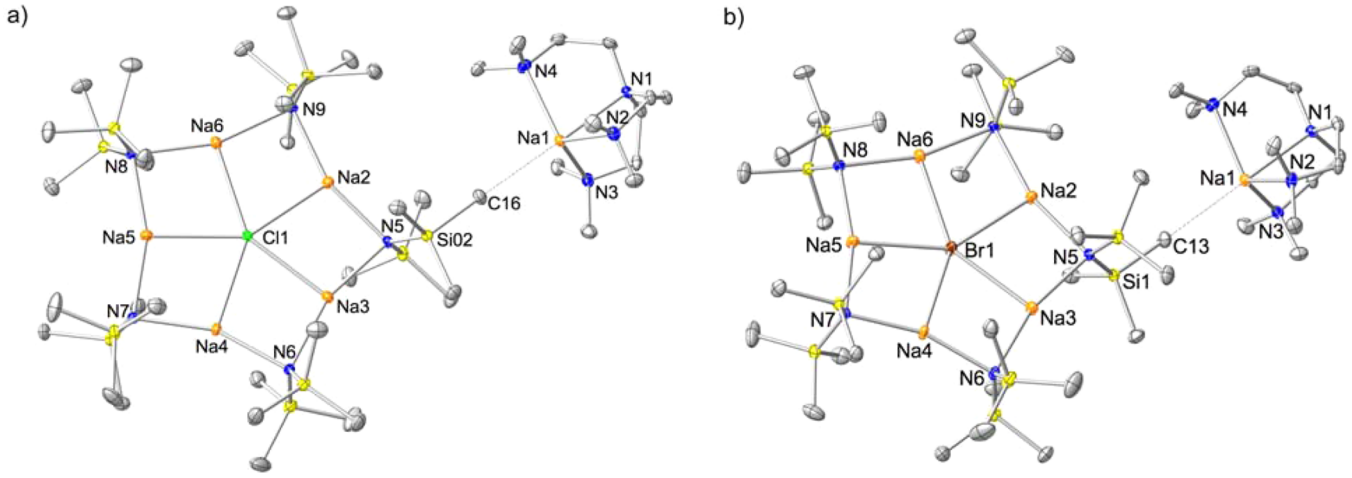

Figure 2. Molecular structures of **1** (a) and **2** (b). H atoms have been omitted for simplicity, and displacement ellipsoids are displayed at 30% probability. The dashed lines illustrate Na···Me agostic interactions. Selected bond distances (Å) and angles (deg) for **1**: Na3−N6 2.368(2), Na3−N5 2.380(2), Na4−N6 2.353(2), Na4−N7 2.352(2), Na5−N7 2.374(2), Na5−N8 2.387(2), Na6−N8 2.391(2), Na6−N9 2.398(2), Na2−N9 2.378(2), Na2−N5 2.384(2), Cl1−Na2 2.7988(12), Cl1−Na4 2.8112(12), Cl1−Na6 2.8302(12), Cl1−Na5 2.8366(12), Cl1−Na3 2.8452(12), N1−Na1 2.455(2), Na1−N4 2.408(2), Na1−N3 2.439(2), Na1−N2 2.443(2), Na1−C16 2.955(3); Na4−N6−Na3 87.88(8), Na4−N7−Na5 88.99(8), Na5−N8−Na6 88.65(8), Na2−N9−Na6 88.99(7), N7−Na4−N6 158.49(8), N7−Na5−N8 161.04(8), N8−Na6−N9 162.05(8), N9−Na2−N5 160.04(8), Na2−Cl1−Na6 72.99(3), Na2−Cl1−Na6 72.99(3), Na4−Cl1−Na5 71.82(3), Na6−Cl1−Na5 72.20(3), Na2−Cl1−Na3 72.16(3), Na4−Cl1−Na3 70.79(3), N4−Na1−C16 104.01(9), N3−Na1−C16 107.03(8), N2−Na1−C16 103.70(8), N1−Na1−C16 177.26(8), N2−Na1−N1 74.14(7), N3−Na1−N1 75.61(7), N4−Na1−N1 75.47(8), N3−Na1−N2 118.94(8), N4−Na1−N3 110.70(9), N4−Na1−N2 111.06(9). Selected bond distances (Å) and angles (deg) for **2**: Na2−N9 2.389(3), Na6−N9 2.414(3), Na6−N8 2.405(3), Na5−N8 2.405(3), Na5−N7 2.387(3), Na4−N7 2.368(3), Na4−N6 2.359(3), Na3−N6 2.380(3), Na3−N5 2.393(3), Na2−N5 2.400(3), Br1−Na2 2.8979(14), Br1−Na4 2.9144(14), Br1−Na5 2.9289(14), Br1−Na6 2.9289(15), Br1−Na3 2.9356(14), Na1−N1 2.452(3), Na1−N4 2.408(3), Na1−N3 2.442(3), Na1−N2 2.444(3), Na1−C13 2.955(4); Na2−N9−Na6 92.29(10), Na5−N8−Na6 91.66(10), Na4−N7−Na5 92.14(10), Na4−N6−Na3 91.23(11), Na3−N5−Na2 91.33(10), N8−Na6−N9 165.30(11), N7−Na5−N8 163.77(11), N6−Na4−N7 162.13(11), N6−Na3−N5 163.48(11), N9−Na2−N5 163.13(11), Na4−Br1−Na5 71.74(4), Na2−Br1−Na6 72.93(4), Na5−Br1−Na6 72.16(4), Na2−Br1−Na3 71.98(4), Na4−Br1−Na3 70.75(4), N4−Na1−C13 104.36(12), N3−Na1−C13 103.61(11), N2−Na1−C13 106.90(11), N1−Na1−C13 177.32(12), N4−Na1−N1 75.50(11), N3−Na1−N1 74.05(10), N2−Na1−N1 75.55(10), N4−Na1−N3 110.63(12), N4−Na1−N2 110.91(12), N3−Na1−N2 119.05(11).

Complexes **1**−**5** all contain an anion that consists of halide-deficient (with respect to amide) pentameric sodium amide rings $[\{Na_5N_5(\mu_5\text{-}X)\}^-]$, where X = Cl (**1**), Br (**2**), and I (**4** and **5**)] with different sodium-based cationic counterions. Complexes **1** and **2** (Figure 2) exist as contacted ion pairs of the type $[\{Na_5(\mu\text{-HMDS})_5(\mu_5\text{-}X)\}\{Na(Me_6TREN)\}]$. The cations in both complexes exhibit similar structural features and contain one Na center four-coordinated to the tetradentate ligand Me_6TREN, giving rise to a $[Na(Me_6TREN)]^+$ ion. This ion, via a Na···C long contact, is bound to the aforementioned anionic ring to generate the corresponding contacted ion-pair complex. The Na···C contacts between the ions in **1** and **2** are composed of long agostic-type interactions[13] between a Me_6TREN-sequestered Na atom and a Me group from an HMDS ligand [Na1···C16 and Na1···C13, both 2.955 Å in **1** and **2**] of the 10-atom anionic ring $[Na_5N_5(\mu_5\text{-}X)]^-$. The Na···C distances in **1** and **2** are similar to those in other complexes containing Na···Me(Me_2)Si interactions (mean distance, 2.97 Å).[14] Containing three donor arms emerging from a central donor, tetraamine Me_6TREN is coordinatively flexible and has displayed all possible η^4, η^3, η^2, and η^1 modes to organoalkali-metal compounds.[15] The donor ligand binds to the metal center in an η^4 fashion in **1** and **2**. The Na center is five-coordinate and adopts a distorted trigonal-bipyramidal geometry. The metal is located in the center of the N(eq) plane of the Me_6TREN ligand. The Na−N(Me_6TREN) bond distances (2.44 Å, mean distance in **1** and **2**) and N−Na−N angles [mean angles, N(eq)−Na1−N(eq) 113.7 and 113.5°, N(eq)−Na1−N(ax) 75.2 and 75.0°, and N(eq)−Na1−C16 104.9° and N(eq)−Na1−C13 106.0°, N(ax)−Na1−C16 177.3°, and N(ax)−Na1−C13 177.3° in **1** and **2**, respectively] are similar to those of other complexes bearing a $[(Me_6TREN)Na]^+$ moiety.[15b,16] The Na atom is 0.63 Å outside of the plane formed by the equatorial N2−N3−N4 atoms (similar to the distance that the Na atom in the Me_6TREN adduct of benzylsodium protrudes from this plane, 0.74 Å)[16c] and is projected toward a Me group of a HMDS ligand.

Contrasting with **1** and **2**, cocomplexes **4** and **5** have solvent-separated structures in the solid state (Figure 3). Note that **4** is the first solid-state structures of an iodide-incorporated metal anionic crown complex. The Na_5N_5 ring appears to be an adequately sized cavity to capture not just chloride and bromide, as for Li_5N_5 rings,[8e] but because of the larger perimeter of the Na_5 ring, the cavity can now accommodate a larger iodide ion. The cation is rather unusual and consists of a Na atom, which bridges two "(PMDETA)NaHMDS" fragments to form $[Na_3(\mu\text{-HMDS})_2(PMDETA)_2]^+$. It is trinuclear in adopting a Na−N(HMDS)−Na−N(HMDS)−Na zigzag chain of atoms. The terminal Na atoms are η^3-coordinated to a PMDETA ligand. This results in the terminal Na atoms adopting a distorted tetrahedral arrangement [mean angles, 116.0, 125.9, and 142.7° for N(HMDS)−Na−N(PMDETA); 73.1, 74.9, and 112.2° for N(PMDETA)−Na−N(PMDETA); mean sum of the N−Na−N angles, 644.8°], while the central Na atom is two-coordinate with a N(HMDS)−Na−N(HMDS) angle of 164.1° (distorted from linearity by 15.9°). A search of the Cambridge Structural Database[17] appears to reveal that this is a unique example of this type of cation.

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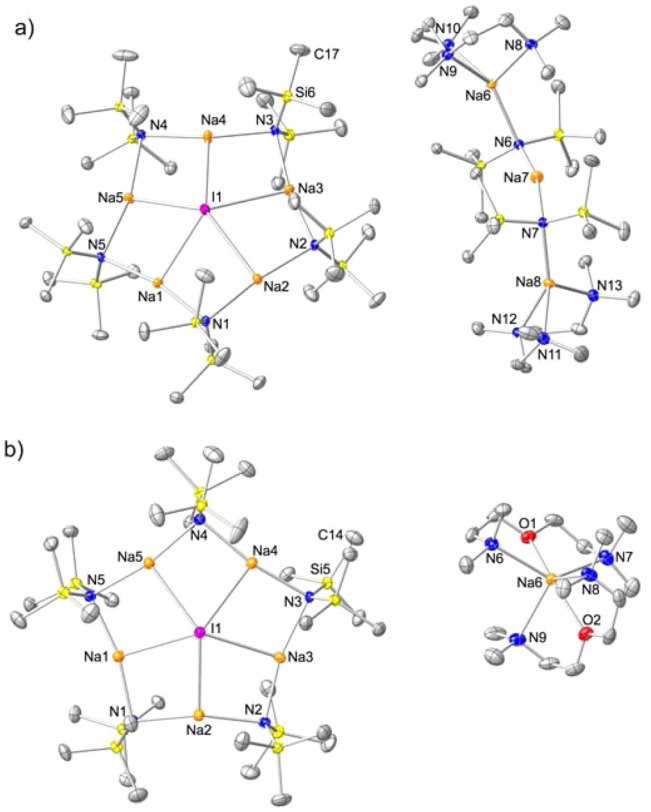

Figure 3. Molecular structures of **4** (a) and **5** (b). For both structures, H atoms have been omitted for clarity. One disordered component of the iodine for 4 and TMDAE for **5** have also been omitted. For **5**, only one molecule from the asymmetric unit is shown. Displacement ellipsoids are displayed at 30% probability. Selected bond distances (Å) and angles (deg) for **4**: Na1−N5 2.424(2), Na5−N5 2.362(2), Na1−N1 2.371(2), Na2−N1 2.397(2), Na2−N2 2.387(2), Na3−N2 2.417(2), Na3−N3 2.428(2), Na4−N3 2.402(2), Na4−N4 2.404(2), Na5−N4 2.408(2), mean Na−I 3.076, Na6−N8 2.533(2), Na6−N9 2.498(2), Na6−N10 2.515(2), Na6−N8 2.533(2), Na6−N6 2.461(2), Na7−N6 2.360(2), Na7−N7 2.406(2), Na8−N7 2.403(2), Na8−N11 2.466(2), Na8−N12 2.518(2), Na8−N13 2.594(2); Na5−N5−Na1 92.89(7), Na1−N1−Na2 97.85(8), Na2−N2−Na3 97.19(8), Na4−N3−Na3 96.54(8), Na4−N4−Na5 95.72(8), N1−Na1−N5 166.98(8), N2−Na2−N1 171.03(8), N2−Na3−N3 169.67(8), N3−Na4−N4 166.71(8), N5−Na5−N4 164.00(8), mean Na−I−Na 70.883, Na7−N6−Na6 108.31(8), Na8−N7−Na7 107.94(8), N6−Na7−N7 164.05(8), N6−Na6−N9 142.53(8), N6−Na6−N10 125.58(7), N9−Na6−N10 74.95(7), N6−Na6−N8 116.00(8), N9−Na6−N8 73.19(7), N10−Na6−N8 112.10(8), N7−Na8−N11 117.31(8), N7−Na8−N12 146.67(8), N11−Na8−N12 75.40(8), N7−Na8−N13 122.01(8), N11−Na8−N13 112.32(8), N12−Na8−N13 72.89(7). Selected bond distances (Å) and angles (deg) for **5**: Na1−N1 2.388(4), Na1−N5 2.377(4), Na2−N1 2.382(4), Na2−N2 2.379(4), Na3−N2 2.406(4), Na3−N3 2.414(4), Na4−N3 2.399(4), Na4−N4 2.435(4), Na5−N4 2.401(4), Na5−N5 2.438(4), I1−Na2 3.105(2), I1−Na4 3.117(2), I1−Na1 3.118(2), I1−Na5 3.123(2), I1−Na3 3.1383(19); Na2−N1−Na196.00(15), Na2−N2−Na3 95.54(15), Na4−N3−Na3 94.95(14), Na5−N4−Na4 98.47(16), N5−Na1−N1 162.79(17), N2−Na2−N1 164.18(17), N2−Na3−N3 166.98(16), N3−Na4−N4 168.38(16), N4−Na5−N5 167.94(16).

Because of the oxophilic nature of alkali metals, we decided to swap the *N*,*N*,*N*-tridentate ligand PMDETA in our reaction with the mixed-donor-atom *N*,*O*,*N*-tridentate ligand TMDAE (Scheme 1). In this case, the Na atom is solvated by two TMDAE molecules, which fully satisfies its coordination sphere to allow formation of the solvent-separated complex **5**. Two independent molecules constitute the asymmetric unit cell of **5**. The anionic parts resemble the same Na_5N_5 structure found in **4**. Both cationic fragments consist of a Na atom coordinated to two TMDAE molecules in a distorted octahedral fashion, where each tridentate TMDAE ligand occupies one distorted octahedral face of the metallic center. This ligand has rarely been reported to coordinate to any alkali metal in the solid state, and only two structures have been previously reported. One of them has TMDAE ligating a Na ion in a η^2 manner in $[(TMDAE)Na(dpa)]_2$ (dpa is 2,2′-dipyridylamide).[18] TMDAE also adopts this chelating mode toward lithium in $[Li(\mu\text{-}Me_2NCH_2CH_2OCHCH_2NMe_2)(\mu\text{-}TMP)Al(^iBu)_2]$, where the bis-amide $LiAl(TMP)_2{}^iBu_2$ additionally deprotonates the Lewis base donor selectively at a position α to the O atom.[19] To the best of our knowledge, **5** represents the first example of an alkali-metal complex coordinating to all three heteroatoms of the TMDAE ligand in the solid state. Only one other example of TMDAE bonding in this way has been reported previously, in the copper(III) complex $[CuCl_3{\cdot}TMDAE]$.[20] Unfortunately, because of disorder within the donor, it is not meaningful to discuss its structural parameters in detail.

The structure of the 10-atom Na_5N_5 ring can be compared with the structural chemistry of salt-free NaHMDS aggregates[21] (e.g., donor-free NaHMDS exists as a zigzag polymeric chain of alternating N and Na atoms[22] and as a near-planar cyclotrimer[23] in the solid state). Complexes **1**−**5** expand the reported lithium amide anionic crowns to sodium and can be considered to resemble inverse crown polymetallic complexes. An inverse crown ether complex (**IV**; Figure 4) is a macrocyclic compound that exhibits an inverse topological relationship to conventional crown ethers (**III**).[24] It is also possible to encapsulate non-oxygen-containing species (such as aryl dianions) within the polymetallic ring, and these are classed as inverse crowns. The main differences between these types of complexes are that alkali-metal anionic crowns (**VI**) are generally solvent-separated or contacted ion pairs that have weak agostic-type interactions holding the ions together, whereas inverse crown ethers/inverse crowns (**IV** and **V**) contain an alkali metal and a divalent metal within a neutral molecule.

The Na_5N_5 anionic cavity in **1**, **2**, **4**, and **5** can be described as a 10-pointed star of alternating Na and N atoms that acts as a homometallic host−guest type complex accommodating a chloride (**1**), a bromide (**2**), or an iodide (**4** and **5**) ion. Only one other anion fragment akin to that in **1** appears to have been crystallographically characterized, namely, the ytterbium amido sodiate complex, $[(Na_5(\mu\text{-}HMDS)_5(\mu_5\text{-}Cl)]^-[L_2Yb]^+$.[25] It can be envisaged that the "star" is constructed of two interpenetrating essentially regular pentagons: one small pentagon composed of five Na atoms and the other a larger pentagon composed of five N atoms. Assuming that the pentagons are concentric, they are disposed at angles of approximately 36° with respect to each other in all of the cases (**1**, **2**, **4**, and **5**; Figure 5a). In order to compare the homometallic sodium amide anionic cavities found for **1**−**5**, structural parameters for the chloride (**1**), bromide (**2**), and iodide (**4** and **5**) derivatives are shown in Table 1, including dimensions related to the aforementioned pentagon cavities.

As expected, the mean Na−μ_5-halogen distance increases in the series Cl < Br < I. The 10-atom Na_5N_5 ring is planar for chloride and bromide, slightly puckered for iodide (mean Na−N−Na−N torsion angles, 170.7, 169.6, and 156.0° in **1**, **2**, and

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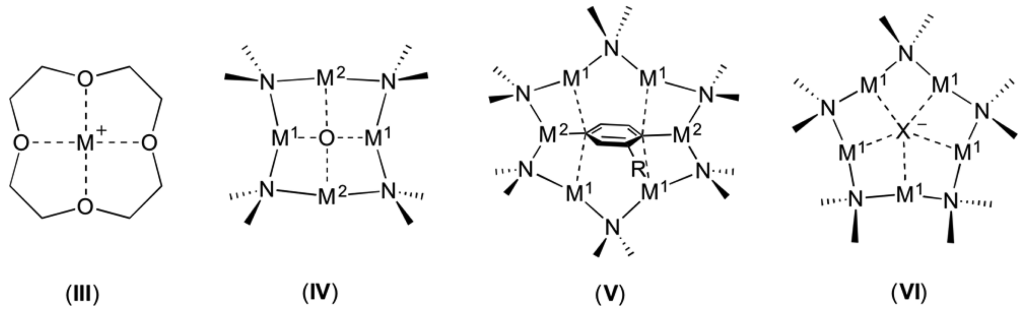

Figure 4. Structures of 12-crown-4 ether (**III**), inverse crown ether (**IV**), inverse crown (**V**), and metal anionic crown (**VI**) complexes.

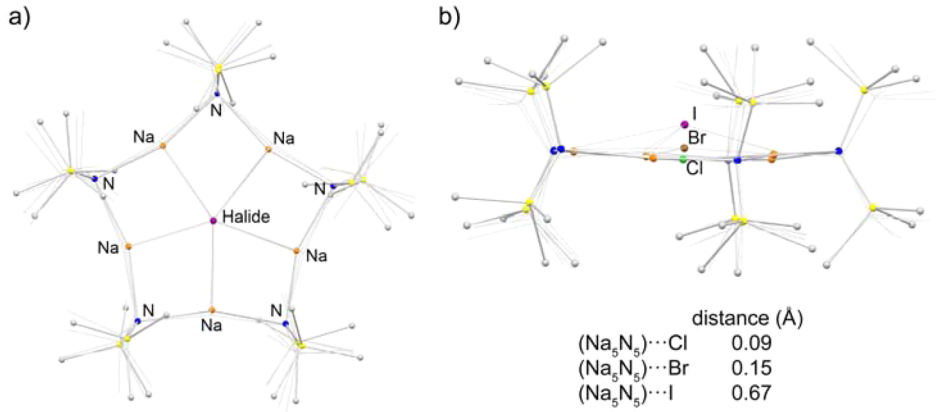

Figure 5. Ball-and-stick superimposed top (a) and side (b) views for the anionic $[Na_5(\mu\text{-HMDS})_5(\mu_5\text{-halide})]^-$ fragments containing chloride (**1**), bromide (**2**), and iodide (**5**). N and Na atoms from **1** have been chosen as references to overlay **2** and **5**.

Table 1. Selected Bond Parameters and Angles for Cocomplexes 1, 2, and 4−7

	1 (Cl)	**2** (Br)	**4** (I)	**5** (I)	**6** (I)	**7** (I)
Na−X[a]	2.82	2.92	3.11	3.10	3.13	3.12
Na−N(HMDS)[a]	2.38	2.39	2.40	2.39	2.39	2.38
Na−X−Na[b]	72.0	71.9	70.3	69.9	67.8	67.3
N(HMDS)−Na−N(HMDS)[b]	160.5	163.6	167.8	166.5	160.3	159.9
Na−N(HMDS)−Na[b]	88.6	91.7	96.1	96.1	93.8	92.6
N_5 pentagon angles[c]	539.3	539.4	538.7	539.4		
Na_5 pentagon angles[c]	539.6	536.7	539.6	539.5		

[a]Mean distance (Å). [b]Mean angle (deg). [c]Sum of the internal angles (540° for a regular pentagon).

5, respectively), but of similar perimeter for **1**−**5**, as judged by comparing the Na−N bond distances (mean Na−N, 2.38−2.40 Å, in **1**−**5**; Table 1). This provides an adequately sized cavity to satisfactorily accommodate chloride, bromide, or iodide ions. Figure 5 shows the different positions that the halide occupies in the planar Na_5N_5 cavity. The halide atoms are geometrically positioned in the center of both concentric pentagons: the chloride ion is approximately coplanar with the 10-atom Na_5N_5 ring (0.09 Å above) in **1**, and the bromide ion is 0.15 Å out of the Na_5N_5 plane in **2**. Chloride and bromide have been previously trapped within a Li_5N_5 ring, but the cavity of Na_5N_5 seems to be of an appropriate size to also accommodate the larger iodide atom in **4** and **5** (Figure 5). The anionic moiety is structurally identical for **4** and **5**, with a 10-atom Na_5N_5 ring hosting an iodide ion that is situated farther from the Na_5N_5 plane (0.67 Å above the plane; Figure 5b) compared with chloride (**1**) and bromide (**2**), suggesting that the Na_5N_5 ring is too small to accommodate the anion in the same plane.

On the basis of the calculated areas, the N_5 pentagon is approximately double the size of the Na_5 pentagon (calculated areas for the Na_5/N_5 pentagons: 19.0/37.8, 20.3/38.5, 21.9/39.1, and 21.8/39.1 Å^2 for **1**, **2**, **4**, and **5**, respectively). The N_5 cores of the complexes are similar in size (mean N···N separation, 4.68, 4.73, 4.77, and 4.77 Å for **1**, **2**, **4**, and **5**, respectively), while the Na_5 cores modestly increase in size with respect to the size of the captured halide, Cl < Br < I (mean Na···Na separations, 3.32, 3.43, 3.57, and 3.55 Å for **1**, **2**, **4**, and **5**, respectively). As expected, the Li_5 cavities of the previously reported complexes, of the form $[Li_5(\mu\text{-HMDS})_5(\mu_5\text{-X})]^-[Li\{(R,R)\text{-TMCDA}\}_2]^+$ (X = Cl and Br), have shorter Li···Li separations and therefore smaller areas for the Li_5 pentagons [mean Li···Li separation (Å)/area (Å^2), 2.86/14.1 (Cl) and 2.97/15.2 (Br)].[8e] In keeping with the results for **1**, **2**, **4**, and **5**, the area of the N_5 pentagon is still approximately twice as large as that of the Li_5 pentagon because of the inherent shortening of the N···N separation. It can be postulated that, because of the relatively small area generated by the Li atoms in the Li_5 cavities, it is not possible to accommodate iodide as a substitute for the bromide ion in the latter complex because it is already 0.4 Å out of the plane.

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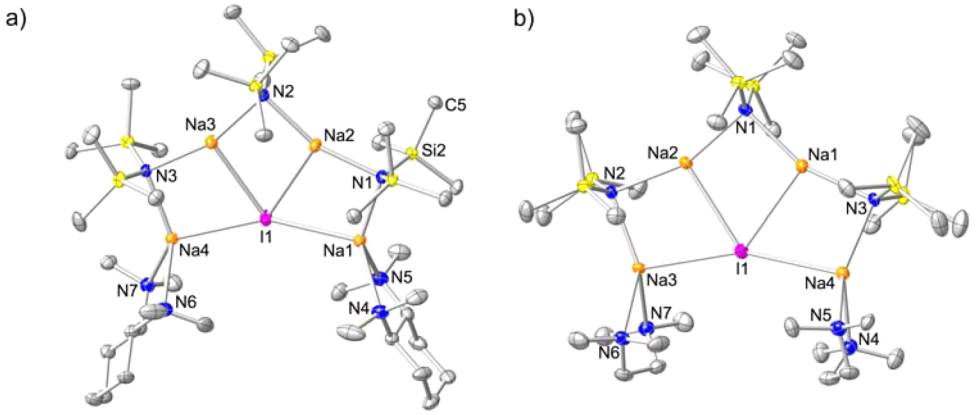

Figure 6. Molecular structures of **6** (a) and **7** (b). H atoms and one disordered component of one TMEDA ligand have been omitted for clarity. Displacement ellipsoids are displayed at 30% probability. Selected bond distances (Å) and angles (deg) for **6**: Na1−N1 2.425(5), Na2−N2 2.369(5), Na2−N1 2.377(5), Na3−N3 2.378(5), Na3−N2 2.382(5), Na4−N3 2.417(5), Na1−N4 2.479(7), Na1−N5 2.528(7), Na4−N7 2.496(6), Na4−N6 2.498(7), Na1−I1 3.128(2), Na2−I1 3.127(2), Na3−I1 3.139(2), Na4−I1 3.123(2); Na2−N1−Na1 94.75(19), Na2−N2−Na3 91.29(17), Na3−N3−Na4 95.29(16), N2−Na2−N1 159.5(2), N3−Na3−N2 160.96(18), Na2−I1−Na1 68.78(6), Na4−I1−Na3 68.94(5), Na2−I1−Na3 65.66(6), N1−Na1−N4 127.1(2), N1−Na1−N5 135.9(2), N4−Na1−N5 70.1(2), N1−Na1−I1 97.65(13), N4−Na1−I1 119.47(18), N5−Na1−I1 106.90(17), N3−Na4−N7 128.4(2), N3−Na4−N6 133.9(3), N7−Na4−N6 70.9(2), N3−Na4−I1 97.56(12), N7−Na4−I1 120.18(16), N6−Na4−I1 105.83(19). Selected bond distances (Å) and angles (deg) for **7**: Na3−N2 2.392(3), Na2−N1 2.383(3), Na2−N2 2.394(3), Na1−N3 2.369(3), Na1−N1 2.384(3), Na4−N3 2.374(3), Na3−N7 2.475(3), Na3−N6 2.491(3), Na4−N4 2.454(4), Na4−N5 2.518(3), Na1−I1 3.1049(15), Na2−I1 3.0964(14), Na3−I1 3.1184(15), Na4−I1 3.1297(14); Na3−N2−Na2 91.45(11), Na2−N1−Na1 93.64(11), Na1−N3−Na4 92.75(12), N1−Na2−N2 159.41(12), N3−Na1−N1 160.47(12), Na2−I1−Na1 68.17(4), Na2−I1−Na3 66.92(4), Na1−I1−Na4 66.82(4), N2−Na3−N7 136.32(12), N2−Na3−N6 135.12(12), N7−Na3−N6 75.99(11), N2−Na3−I1 100.53(8), N7−Na3−I1 96.01(9), N6−Na3−I1 106.09(9), N3−Na4−N4 138.38(12), N3−Na4−N5 133.18(12), N4−Na4−N5 75.78(11), N3−Na4−I1 99.61(9), N4−Na4−I1 101.20(9), N5−Na4−I1 102.59(9).

We also studied the influence of the denticity of the Lewis base donor of choice on the formation of these halogen-deficient sodium anionic ring complexes by replacing the tetradentate Me_6TREN and tridentate PMDETA and TMDAE donors with the bidentate (*R*,*R*)-TMCDA and TMEDA ligands. Cocomplexes **6**−**8** crystallized in the monoclinic crystal system, and they are found to have similar structures consisting of a Na_4N_3 chain, with the two terminal metal centers each being coordinated to bidentate ligand (*R*,*R*)-TMCDA (**6**) or TMEDA (**7** and **8**) (Figures 6 and 7). The employment of these donors produced three essentially isostructural complexes, structures that contained a novel neutral "open ring" motif, with the general formula $[Na_4(\mu\text{-HMDS})_3(\mu_4\text{-X})(\text{donor})_2]$ [donor = (*R*,*R*)-TMCDA and X = I for **6**; donor = TMEDA and X = I for **7**; donor = TMEDA and X = Br for **8**]. It can be envisaged that a tetranuclear sodium amide chain acts as a host toward iodide (**6** and **7**) or bromide (**8**) ions.

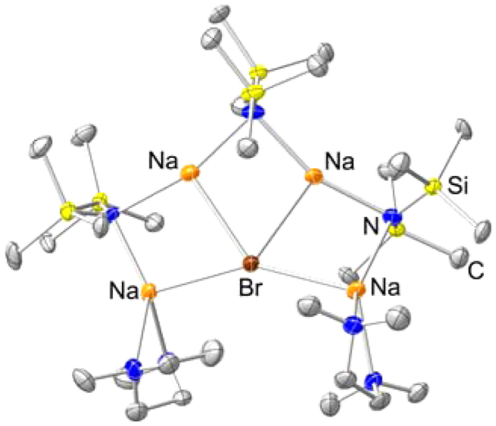

Figure 7. Molecular structure of **8** displaying its atom connectivity. H atoms and disordered components of TMEDA and HMDS ligands have been omitted for clarity. Displacement ellipsoids are displayed at 30% probability.

The Na_4N_3 chain is essentially planar, and the iodide ion occupies a position 0.26 Å out of the plane containing the Na−N−Na−N−Na−N−Na chain in **6**, while it is almost coplanar in **7** (0.07 Å above). This is perhaps due to the more constrained and less flexible nature of (*R*,*R*)-TMCDA, forcing the halide further away from the Na_4N_3 plane. In both cases, the corresponding bidentate ligands are η^2-coordinated to the two terminal Na atoms, rendering them four-coordinated. The separations between the terminal Na atoms (Na4···Na1 and Na4···Na3, 6.10 and 6.14 Å in **6** and **7**, respectively; Figure 6) are longer than the analogous Na···Na separations in **4** and **5** (mean Na···Na separation, 5.77 Å; Figure 3). The open-ring, more flexible nature of **6** and **7** means that the Na_4 cavity can accommodate an iodide ion more easily, and thus it protrudes less from the metal plane. The Na−I bond distances are similar in **6** and **7** (mean Na−I distances, 3.13 and 3.11 Å, respectively; Table 1) and to those found in the solvent-separated complexes **4** and **5** (3.11 and 3.10 Å, respectively), being shorter than the shortest Na−I distances in NaI salt itself (3.231 Å), albeit that the sodium and iodine coordination numbers in **4** and **5** are lower than those encountered in NaI.[26] The diglyme and 18-crown-6 adducts of sodium iodide [NaI(L), where L = $(CH_3OCH_2CH_2)_2O$ or 18-crown-6] present Na−I bond lengths similar to those in complexes **4**−**7** (3.164 and 3.138 Å, respectively).[27] The Na−N(HMDS) and Na−N(donor) dimensions **6** and **7** are similar [mean Na−N(HMDS)/Na−N(donor) distance, 2.39/2.50 and 2.38/2.49 Å, respectively], and as expected, in both compounds, the Na−N(amine) bonds are longer than the Na−N(amide) bonds.[28] The two terminal Na atoms in **6** and **7** have distorted tetrahedral coordination spheres [range of angles, 70.10(2)−135.90(2)° for Na1 and 70.90(2)−133.9(3)° for Na4 in **6**; 75.99(11)−136.32(12)° for

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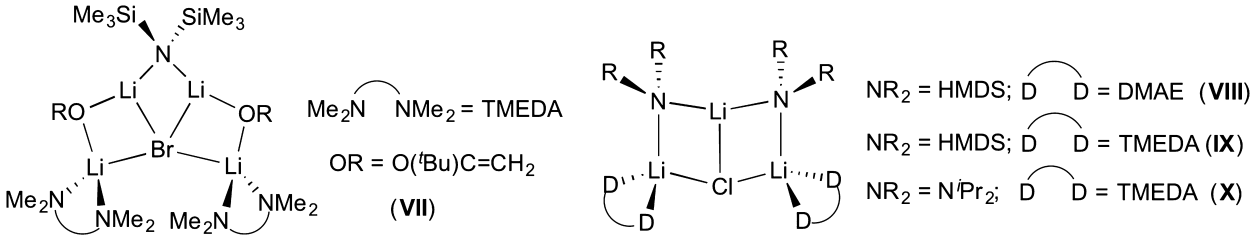

Figure 8. Structural representations of the [(LiBr)(TMEDA$_2$(LiOR)$_2$LiHMDS)] (**VII**) and [(LiCl)(donor·LiNR$_2$)$_2$] (**VIII**–**X**) reagents.

Na3 and 75.78(11)–138.38(12)° for Na4 in **7**] primarily because of the acute bite angle of the bidentate ligand when coordinating to the Na atom. In an attempt to extend the scope of the reaction employed in the preparation of **7**, NaBr was utilized instead of NaI. This produced **8**, but because of disorder, the structural parameters cannot be discussed in detail (Figure 7).

Some lithium-containing structures that are related to **6**–**8** have been reported. During investigations into enolization and addition reactions, Williard et al. isolated a tetralithium mixed amido/enolate/bromide complex, [(LiBr)·(TMEDA$_2$(LiOR)$_2$LiHMDS)] (**VII**, where OR is OC(^{t}Bu)=CH$_2$; Figure 8),[29] which closely resembles the metal–anion framework of **6**–**8**. Also related to this work are the trilithium amide/chloride structures [(LiCl)(donor·LiNR$_2$)$_2$] [NR$_2$ = HMDS, DA; donor = TMEDA and DMAE [2-(*N*,*N*-dimethylamino)ethyl methyl ether], which formally contain one unit less of MNR$_2$ to complete the structure (**VIII**–**X**; Figure 8).[8b,c]

NMR Spectroscopic Studies. Compounds **1**–**8** were characterized by ^{1}H and ^{13}C NMR spectroscopy. All of the reactions in which cesium halides were used as reactants led to the formation of CsHMDS/MX (where M = Na or Cs) cocomplexes as byproducts via partial salt metathesis. This was confirmed by ^{133}Cs NMR spectroscopic studies of the corresponding reaction mixtures.[30] The NMR spectroscopic data for a genuine sample of [(Me$_6$TREN)CsHMDS] were significantly different from those of the byproducts above, likely indicating the incorporation of metal halide salts. Full details can be found in Figures S22–S26 .

Cocomplexes **1**–**5** are poorly soluble in C$_6$D$_6$ and toluene-d_8 solvents at ambient temperature, while cocomplexes **6**–**8** display good solubility in C$_6$D$_6$ at ambient temperature. Therefore, ^{1}H and ^{13}C NMR spectroscopic experiments utilizing more polar tetrahydrofuran (THF)-d_8 solutions were undertaken for **1**–**5**, presumably at the cost of altering the aggregation state found in the respective solid-state structures and resulting in the preclusion of dynamic equilibrium. In an effort to study the solution state of **5** in a less polar and less coordinating toluene-d_8 solvent, ^{1}H and ^{13}C NMR spectroscopic studies of **5** were additionally studied at 363 K, the temperature at which a homogeneous solution was observed. The ^{1}H and ^{13}C NMR spectra of **1**–**8** in their respective solvents were relatively simple, and the resonances were limited to two distinct regions corresponding to the Lewis base donor of choice and the HMDS ligand present in the corresponding complex.

^{1}H NMR spectra obtained for THF-d_8 solutions of **1**–**3** are coincident and show resonances for an uncoordinated Me$_6$TREN ligand. Altering the sodium halide (Cl, Br, and I) salts has little effect on the ^{1}H and ^{13}C chemical shifts of both Me$_6$TREN and HMDS ligands in **1**–**3**. Moreover, the observed chemical shifts for Me$_6$TREN and HMDS ligands in **1**–**3** in THF-d_8 are similar to those found for a salt-free sample of Me$_6$TREN·NaHMDS[31] in the same solvent for which a total dissociation of Me$_6$TREN from the metal amide complex is also observed,[32] presumably because of the high coordinating ability of the vast excess of THF-d_8, breaking the structure found in the solid state. The Me$_6$TREN/HMDS ratio found was approximately 1:5, as expected from the solid-state structure of **1**–**3**.

Looking at the solvent-separated complexes **4** and **5**, ^{1}H and ^{13}C NMR spectra in THF-d_8 show the corresponding resonances for HMDS and Lewis base (PMDETA and TMDAE, respectively) ligands at the same chemical shifts as those for "(THF-d_8)·NaHMDS" and noncoordinated PMDETA or TMDAE ligands for **4** and **5**, respectively (Tables S3 and S4). In addition, PMDETA/HMDS and TMDAE/HMDS ratios of approximately 1:3.5 and 1:2.5 are found for **4** and **5**, respectively, being in agreement with the proportions found in the solid-state structures. In an attempt to study the unaltered structure for **5** in solution, ^{1}H and ^{13}C NMR spectroscopic studies of **5** in toluene-d_8 at 363 K were carried out as **5** is soluble in toluene-d_8 at this temperature. Under these conditions, the chemical shifts for the TMDAE and HMDS groups are coincident with those of an in situ prepared sample of TMDAE·NaHMDS in toluene-d_8 at the same temperature (Table S4), suggesting that the sodium halide present in the structure of **5**, which is silent by NMR spectroscopy, has a marginal effect on the chemical shifts of both NaHMDS and free TMADE ligands compared to those of TMDAE·NaHMDS.

^{1}H and ^{13}C NMR spectroscopic studies of **6**–**8** in C$_6$D$_6$ solutions reveal that the resonances for the bidentate Lewis base [i.e., (*R*,*R*)-TMCDA and TMEDA] have been shifted upfield with respect to the free donor because of coordination to the electropositive sodium metal (Tables S5 and S8). In contrast, a downfield shift in the ^{1}H signals is observed for the HMDS groups in **6**–**8** (0.41, 0.36, and 0.35 ppm for **6**–**8**, respectively) compared with C$_6$D$_6$ solutions of (*R*,*R*)-TMCDA·NaHMDS, [(TMEDA)(NaHMDS)$_2$]$_\infty$,[33] and NaHMDS (0.35, 0.19, and −0.19 ppm, respectively). If the solution-state chemistry for **6**–**8** mirrors that of the solid state, then two different resonances for the HMDS ligand should exist because of the different chemical environments present. Looking specifically at **7**, at 300 K for a toluene-d_8 solution of the complex, this is not the case: only one resonance at 0.28 ppm is observed. However, upon cooling of the solution, significant resonance broadening is observed and the resonance drifts downfield (at 253 K, 0.37 ppm). At 233 K, a shoulder (0.25 ppm) appears on the main resonance (0.44 ppm). At 223 K, two distinct resonances are observed (at 0.47 and 0.27 ppm) in a 2:1 integral ratio, which is consistent with the solid-state

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structure of **7**. It was also noted that the solubility of **7** decreased markedly in toluene-d_8 at lower temperatures.

Previously, it was noted that **7** could be prepared and crystallized from a solution containing an excess of NaHMDS. It was decided to probe the solution structure (hence stability) of **7** in the presence of an excess of NaHMDS. A total of 1, 2, and 3 equiv of NaHMDS were added to 1 equiv of **7** in a C_6D_6 solution (Figure S18). Upon the addition of 1 equiv of NaHMDS, only one HMDS resonance was observed (0.29 ppm). This signal could not be attributed to free NaHMDS (or indeed a TMEDA solvate of NaHMDS; the previously reported diamine solvate (TMEDA)NaHMDS has a HMDS chemical shift of 0.19 ppm).[33] Instead, one HMDS resonance gradually drifted upfield from 0.36 ppm (when no additional NaHMDS is added) to 0.21 (when an additional 3 equiv of NaHMDS is added). Interestingly, the two resonances for TMEDA [at 2.01 (CH_3) and 1.81 (CH_2) ppm] remain consistent throughout the series of experiments and differ significantly from those in (TMEDA)NaHMDS [1.99 (CH_2) and 1.97 (CH_3) ppm]. These data therefore suggest that the additional NaHMDS is in fast dynamic exchange with the NaHMDS units within the open-ring framework of **7**. This suggests that **7** does not incorporate further NaHMDS units to generate a metal anionic crown motif akin to **3**−**5**. If this were to occur, it is likely that the TMEDA environment in such a species would differ significantly from that found in **7**. These data help to explain why **7** can be crystallized from a solution containing an excess of NaHMDS [i.e., **7** is less soluble in an arene solution than (TMEDA)NaHMDS].

Providing further evidence for these conclusions, 1, 2, and 3 equiv of TMEDA were added to 1 equiv of **7** in a C_6D_6 solution (Figure S19). Here the HMDS resonance remains essentially constant throughout (0.37−0.39 ppm); however, the TMEDA resonances change significantly, ranging from 2.01 (CH_3) and 1.81 (CH_2) ppm for **7** to 2.08 (CH_3) and 2.14 (CH_2) for **7** with an additional 3 equiv of TMEDA. It can be envisaged that adding a large excess of TMEDA could deaggregate **7** because there are two formally unsolvated Na ions present. However, because the HMDS signal remains constant, it seems that the open-ring framework is staying intact. The TMEDA ligands initially attached to the Na atoms in **7** appear to be in dynamic equilibrium with the excess TMEDA.

CONCLUSIONS

In summary, we report the synthesis of a family of chloro- (**1**), bromo- (**2**), and iodo-deficient (**3**) NaHMDS complexes by salt metathesis of an excess of NaHMDS with the corresponding cesium halide salt in the presence of the tetradentate Me_6TREN ligand. The halide is trapped within a pentameric cavity of NaHMDS, while Me_6TREN formally η^4-coordinates to the Na^+ counterion, enabling formation of the corresponding contacted ion-pair complexes with long agostic-type Na···Me(HMDS) interactions. When a tridentate Lewis base is used, the solvent-separated cocomplexes **4** and **5** are obtained in which an iodide ion is trapped by formal ionization of NaI with NaHMDS in the presence of PMDETA and TMDAE, respectively. Upon switching to bidentate ligands [(*R*,*R*)-TMCDA and TMEDA], novel open-ring cocomplexes **6**−**8** were obtained instead of Na_5N_5 closed-ring species. In short, our X-ray diffraction studies provide useful structural insights into the aggregation state of NaHMDS with NaCl, NaBr, and NaI in the presence of Lewis donor ligands of different nature and denticity.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under a protective dry argon atmosphere using standard Schlenk techniques. *n*-Hexane and toluene were distilled under reflux within a nitrogen atmosphere in the presence of sodium metal and benzophenone. In addition, toluene was stored under argon over activated molecular sieves (4 Å) prior to use. C_6D_6 and toluene-d_8 were degassed and stored under argon over activated molecular sieves (4 Å) prior to use. THF-d_8 was degassed, dried, and stored under argon over a potassium mirror prior to use. *n*-BuNa was prepared according to literature methods and stored in a glovebox.[34] 1,1,1,3,3,3-Hexamethyldisilazane [HMDS(H)], *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and *N*,*N*,*N*′,*N*′-tetramethyldiaminoethyl ether (TMDAE) were purchased from Aldrich, distilled under a nitrogen atmosphere in the presence of CaH_2, and stored under argon over activated molecular sieves (4 Å). Tris[2-(dimethylamino)ethyl]amine (Me_6TREN) and *N*,*N*,*N*′,*N*′-(*R*,*R*)-tetramethylcyclohexane-1,2-diamine [(*R*,*R*)-TMCDA] were prepared according to literature methods[35] and stored under argon over activated molecular sieves (4 Å). CsCl, CsBr, and CsI were purchased from Aldrich, dried under vacuum at 150 °C for 5 days, and stored in a glovebox. NH_4Br, NaBr, and NaI were purchased form Aldrich, dried under vacuum at 150 °C for 2 days, 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 NMR, 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; however, for **2**−**4**, variable values were obtained because of the high reactivity of the sodium sodiate species.

*Synthesis of [{Na$_5$(μ-HMDS)$_5$(μ_5-Cl)}{Na(Me_6TREN)}] (**1**).* *n*-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL), and HMDS(H) (1.26 mL, 6 mmol) was added via a syringe to give a white suspension, which was stirred for 3 h. CsCl (168 mg, 1 mmol) was added using a solid addition tube to give a light-brown suspension, which was stirred for 24 h. Me_6TREN (0.53 mL, 2 mmol) was then added via syringe, and the reaction mixture was stirred for 24 h. Toluene (10 mL) was then added, the reaction mixture was heated with a heat gun, and the hot reaction mixture was then filtered to give an orange solution. The solvent was partially removed under vacuum (4 mL), and **1** was crystallized as colorless crystals suitable for an X-ray diffraction study, allowing the hot solution to cool for 24 h in a Dewar containing hot water. **1** was filtered, washed with *n*-hexane (10 mL), and dried under vacuum for 30 min. Yield: 470 mg, 0.39 mmol, 39%. ^{1}H NMR (400.1 MHz, THF-d_8, 300 K): δ −0.20 (br s, 90 H, Me_3Si), 2.16 (br s, 18 H, *Me*$_6$TREN), 2.31 (t, 6 H, $^3J_{HH}$ = 6.8 Hz, CH_2, Me_6TREN), 2.55 (t, 6 H, $^3J_{HH}$ = 6.8 Hz, CH_2, Me_6TREN). ^{13}C{^{1}H} NMR (100.6 MHz, THF-d_8, 300 K): δ 6.6 (Me_3Si), 46.0 (*Me*$_6$TREN), 53.9 (α-CH_2, Me_6TREN), 58.8 (β-CH_2, Me_6TREN). Anal. Calcd (found) for $C_{42}H_{119}ClN_9Na_6Si_{10}$: C, 41.84 (42.40); H, 10.03 (10.23); N, 10.46 (10.87).

*Synthesis of [{Na$_5$(μ-HMDS)$_5$(μ_5-Br)}{Na(Me_6TREN)}] (**2**).* **Method A**. *n*-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL), and bis(trimethylsilyl)amine (1.26 mL, 6 mmol) was added via syringe to give a white suspension, which was stirred for 3 h. CsBr (213 mg, 1 mmol) was added using a solid addition tube to give a pale-orange suspension, which was stirred for 24 h. Me_6TREN (0.53 mL, 2 mmol) was then added via syringe, and the reaction mixture was stirred for 24 h. The solvent was removed under vacuum until dryness to give a light-brown residue from which **2** was extracted with hot toluene (10 mL) to give a light-yellow solution. The solvent was removed under vacuum until dryness, and **2** was crystallized as colorless block crystals suitable for an X-ray diffraction study from a 1:1.6 mixture of toluene/*n*-hexane (6.5 mL) at −25 °C for 24 h. **2** was filtered, washed with *n*-hexane (10 mL), and dried under vacuum for 30 min. Yield: 490 mg, 0.39 mmol, 39%. **Method B**. *n*-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL), and

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bis(trimethylsilyl)amine (1.05 mL, 5 mmol) was added via a syringe to give a white suspension, which was stirred for 3 h. NH_4Br (98 mg, 1 mmol) was then added using a solid addition tube to give a light-orange suspension, which was stirred for 24 h. Me_6TREN (0.53 mL, 2 mmol) was then added via a syringe, and the reaction mixture was stirred for 24 h. Then, toluene (10 mL) was added, the reaction mixture was heated with a heat gun, and the hot reaction mixture was filtered to give an orange solution. The solvent was removed under vacuum until dryness, and **2** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 2:1 mixture of *n*-hexane/toluene (6 mL) at −25 °C for 24 h. **2** was filtered, washed with *n*-hexane (5 mL), and dried under vacuum for 30 min. **2** was filtered, washed with *n*-hexane (2 mL), and dried under vacuum for 30 min. Yield: 230 mg, 0.18 mmol, 18%. **Method C**. *n*-Butylsodium (401 mg, 5 mmol) was suspended in *n*-hexane (20 mL), and bis(trimethylsilyl)-amine (1.05 mL, 5 mmol) was added via a syringe to give a white suspension, which was stirred for 3 h. NaBr (103 mg, 1 mmol) was then added using a solid addition tube, and the reaction mixture was stirred for 24 h. Me_6TREN (0.54 mL, 2 mmol) was then added to give a light-brown suspension, which was stirred for 24 h. The solvent was removed under vacuum until dryness to give a pale-brown residue from which **2** was extracted in hot toluene (10 mL) to give a pale-yellow solution. The solvent was removed under vacuum until dryness, and **2** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 1:1 mixture of *n*-hexane/toluene (4 mL) at −25 °C for 24 h. **2** was filtered, washed with *n*-hexane (2 mL), and dried under vacuum for 30 min. Yield: 130 mg, 0.10 mmol, 10%. NMR spectroscopy and X-ray diffraction studies of the crystalline sample isolated in methods A−C proved that the compound was **2**. ^1H NMR (400.1 MHz, THF-d_8, 300 K): δ −0.19 (br s, 90 H, Me_3Si), 2.18 (br s, 18 H, Me_6TREN), 2.32 (t, 6 H, $^3J_{HH}$ = 6.6 Hz, CH_2, Me_6TREN), 2.55 (t, 6 H, $^3J_{HH}$ = 6.8 Hz, CH_2, Me_6TREN). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 6.6 (Me_3Si), 46.0 (Me_6TREN), 53.5 (α-CH_2, Me_6TREN), 58.6 (β-CH_2, Me_6TREN). Anal. Calcd (found) for $C_{42}H_{119}BrN_9Na_6Si_{10}$: C, 40.35 (41.27); H, 9.67 (9.81); N, 10.08 (10.21).

*Synthesis of [{$Na_5(\mu$-HMDS)$_5(\mu_5$-I)}{Na(Me_6TREN)}] (**3**).* *n*-Butylsodium (480 mg, 6 mmol) was suspended in *n*-hexane (20 mL), and bis(trimethylsilyl)amine (1.26 mL, 6 mmol) was added via a syringe to give a white suspension, which was stirred for 3 h. CsI (260 mg, 1 mmol) was then added using a solid addition tube, and the reaction mixture was stirred for 24 h. Me_6TREN (0.52 mL, 2 mmol) was then added via a syringe to give a light-brown suspension, which was stirred for 60 h. The solvent was removed under vacuum to give a light-brown residue, from which **3** was extracted in hot toluene (10 mL) to give a light-yellow solution. The solvent was removed under vacuum until dryness, and **3** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 1:1.25 mixture of *n*-hexane/toluene (4.5 mL) at −25 °C for 24 h. Yield: 460 mg, 0.35 mmol, 35%. ^1H NMR (400.1 MHz, THF-d_8, 300 K): δ −0.19 (br s, 90 H, Me_3Si), 2.23 (br s, 18 H, Me_6TREN), 2.36 (br t, 6 H, $^3J_{HH}$ = 6.0 Hz, CH_2, Me_6TREN), 2.52 (br t, 6 H, $^3J_{HH}$ = 6.0 Hz, CH_2, Me_6TREN). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 6.6 (Me_3Si), 45.7 (Me_6TREN), 52.5 (α-CH_2, Me_6TREN), 58.0 (β-CH_2, Me_6TREN). Anal. Calcd (found) for $C_{42}H_{119}IN_9Na_6Si_{10}$: C, 38.89 (39.47); H, 9.32 (9.57); N, 9.72 (9.95).

Note that the NMR spectroscopic data for **1**−**3** are identical.

*Synthesis of [$Na_5(\mu$-HMDS)$_5(\mu_5$-I)][$Na_3(\mu$-HMDS)$_2$(PMDETA)$_2$] (**4**).* *n*-Butylsodium (560 mg, 7 mmol) suspended in *n*-hexane (20 mL) and bis(trimethylsilyl)amine (1.47 mL, 7 mmol) was added via a syringe to give a white suspension, which was stirred for 2 h. NaI (150 mg, 1 mmol) was then added using a solid addition tube, and the reaction mixture was stirred for 24 h. PMDETA (0.42 mL, 2 mmol) was added via a syringe, and the resulting brown suspension was stirred for 15 h. The solvent was removed under vacuum until dryness to give a pale-brown residue, from which **4** was extracted in hot toluene (20 mL) to give a pale-yellow solution. The solvent was removed under vacuum until dryness, and **4** was crystallized as colorless crystals suitable for an X-ray diffraction study from *n*-hexane (2 mL) at −25 °C for 24 h. Yield: 630 mg, 0.35 mmol, 35%. ^1H NMR (400.1 MHz, THF-d_8, 300 K): δ −0.19 (s, 63 H, Me_3Si), 2.18 (s, 12 H, Me_2N, PMDETA), 2.22 (s, 3 H, MeN, PMDETA), 2.33 (t, 4 H, $^3J_{HH}$ = 6.4 Hz, CH_2, PMDETA), 2.42 (t, 4 H, $^3J_{HH}$ = 6.4 Hz, CH_2, PMDETA). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 6.8 (Me_3Si), 43.5 (MeN, PMDETA), 46.2 (Me_2N, PMDETA), 57.0 (CH_2, PMDETA), 58.6 (CH_2, PMDETA). Anal. Calcd (found) for $C_{60}H_{172}IN_{13}Na_8Si_{14}$: C, 40.48 (41.04); H, 9.74 (9.67); N, 10.23 (11.01).

*Synthesis of [$Na_5(\mu$-HMDS)$_5(\mu_5$-I)][Na(TMDAE)$_2$] (**5**).* *n*-Butylsodium (401 mg, 5 mmol) was suspended in *n*-hexane (20 mL), and bis(trimethylsilyl)amine (1.05 mL, 5 mmol) was added via a syringe to give a white suspension, which was stirred for 2 h. NaI (150 mg, 1 mmol) was then added using a solid addition tube, and the reaction mixture was stirred for 24 h. TMDAE (0.38 mL, 2 mmol) was then added via a syringe, and the reaction mixture was stirred for 15 h. The solvent was removed under vacuum until dryness to give white residue, from which **5** was extracted with hot toluene (30 mL) to give a pale-yellow solution. The solvent was removed under vacuum until dryness, and **5** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 2:1 mixture of *n*-hexane/toluene (3 mL) at −25 °C for 24 h. Yield: 480 mg, 0.36 mmol, 36%. ^1H NMR (400.1 MHz, THF-d_8, 300 K): δ −0.19 (br s, 45 H, Me_3Si), 2.20 (s, 12 H, Me TMDAE), 2.42 (t, 4 H, $^3J_{HH}$ = 6.0 Hz, NCH_2, TMDAE), 3.49 (t, 4 H, $^3J_{HH}$ = 6.0 Hz, OCH_2, TMDAE). ^1H NMR (400.1 MHz, toluene-d_8, 363 K): δ 0.16 (s, 45 H, Me_3Si), 1.99 (s, 12 H, Me-TMDAE), 2.01 (t, 4 H, $^3J_{HH}$ = 5.2 Hz, NCH_2, TMDAE), 2.92 (t, 4 H, $^3J_{HH}$ = 5.2 Hz, OCH_2, TMDAE). $^{13}C\{^1H\}$ NMR (100.6 MHz, THF-d_8, 300 K): δ 6.7 (Me_3Si), 46.1 (Me TMDAE), 59.8 (NCH_2, TMDAE), 68.8 (OCH_2, TMDAE). $^{13}C\{^1H\}$ NMR (100.6 MHz, toluene-d_8, 363 K): δ 7.0 (Me_3Si), 45.0 (Me, TMDAE), 58.8 (NCH_2), 67.0 (OCH_2). Anal. Calcd (found) for $C_{46}H_{130}IN_9Na_6O_2Si_{10}$: C, 39.83 (40.27); H, 9.45 (9.45); N, 9.02 (9.37).

*Synthesis of [$Na_4(\mu$-HMDS)$_3(\mu_4$-I){(R,R)-TMCDA)}$_2$] (**6**).* *n*-Butylsodium (240 mg, 3 mmol) was suspended in *n*-hexane (20 mL), and bis(trimethylsilyl)amine (0.63 mL, 3 mmol) was added via a syringe to give a white suspension, which was stirred for 2 h. NaI (150, 1 mmol) was added via an addition tube, and the reaction mixture was stirred for 24 h. (*R*,*R*)-TMCDA (0.39 mL, 2 mmol) was then added via a syringe, and the reaction mixture was stirred for 15 h to give a yellow suspension. The solvent was removed under vacuum until dryness to give a yellow residue, from which **6** was extracted in hot toluene (30 mL) to give a yellow solution. The solvent was removed under vacuum, and **6** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 3:5 mixture of *n*-hexane/toluene (8 mL) at −25 °C for 24 h. Colorless crystals grew after 24 h. **6** was filtered, washed with *n*-hexane (5 mL), and dried under vacuum for 30 min. Yield: 330 mg, 0.32 mmol, 32%. ^1H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.41 (s, 27 H, Me_3Si), 0.69 [br s, 4 H, CH_2, (*R*,*R*)-TMCDA], 1.42 [br s, 4 H, CH_2, (*R*,*R*)-TMCDA], 2.00 [br s, 2 H, CH, (*R*,*R*)-TMCDA], 2.12 [br s, 12 H, Me, (*R*,*R*)-TMCDA]. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ 7.5 (Me_3Si), 21.5 [CH_2, (*R*,*R*)-TMCDA], 25.3 [CH_2, (*R*,*R*)-TMCDA], 41.0 [v br s, CH, (*R*,*R*)-TMCDA], 63.7 [Me, (*R*,*R*)-TMCDA]. Anal. Calcd (found) for $C_{38}H_{98}IN_7Na_4Si_6$: C, 43.86 (43.45); H, 9.49 (9.03); N, 9.42 (9.31).

*Synthesis of [$Na_4(\mu$-HMDS)$_3(\mu_4$-I)(TMEDA)$_2$] (**7**).* *n*-Butylsodium (240 mg, 3 mmol) was suspended in *n*-hexane (20 mL), and bis(trimethylsilyl)amine (0.63 mL, 3 mmol) was added via a syringe to give a white suspension, which was stirred for 2 h. NaI (150 mg, 1 mmol) was added via an addition tube, and the reaction mixture was stirred for 24 h. TMEDA (0.3 mL, 2 mmol) was added via a syringe to give a dark-yellow suspension, which was stirred for 15 h. The solvent was partially removed under vacuum (15 mL), and toluene (30 mL) was added. The reaction was heated with a heat gun, and the hot reaction mixture was filtered to give a yellow solution. The solvent was removed under vacuum until dryness, and **7** was crystallized as colorless crystals suitable for an X-ray diffraction study from a 3:5 mixture of *n*-hexane/toluene (8 mL) at −25 °C for 24 h. **7** was filtered, washed with *n*-hexane (5 mL), and dried under vacuum for 30 min. Yield: 410 mg, 0.44 mmol, 44%. ^1H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.36 (s, 27 H, Me_3Si), 1.81 (s, 4 H, CH_2, TMEDA), 2.01 (s, 12 H, Me, TMEDA). ^1H NMR (400.1 MHz, toluene-d_8, 300 K): δ 0.28 (s, 27 H, Me_3Si), 1.85 (s, 4 H, CH_2, TMEDA), 2.03 (s, 12 H, Me,

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TMEDA). ^{1}H NMR (400.1 MHz, toluene-d_8, 253 K): δ 0.37 (s, 27 H, Me_3Si), 1.73 (s, 4 H, CH_2, TMEDA), 1.98 (s, 12 H, Me, TMEDA). ^{1}H NMR (400.1 MHz, toluene-d_8, 233 K): δ 0.25 (bs, 9 H, Me_3Si), 0.44 (bs, 18 H, Me_3Si), 1.68 (s, 4 H, CH_2, TMEDA), 1.96 (s, 12 H, Me, TMEDA). ^{1}H NMR (400.1 MHz, toluene-d_8, 223 K): δ 0.27 (bs, 9 H, Me_3Si), 0.47 (bs, 18 H, Me_3Si), 1.63 (s, 4 H, CH_2, TMEDA), 1.96 (s, 12 H, Me, TMEDA). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ 7.2 (Me_3Si), 46.4 (Me, TMEDA), 57.2 (CH_2, TMEDA). Anal. Calcd (found) for $C_{30}H_{86}IN_7Na_4Si_6$: C, 38.64 (38.71); H, 9.30 (9.04); N, 10.52 (11.23).

*Synthesis of [Na_4(μ-HMDS)$_3$(μ_4-Br)(TMEDA)$_2$] (**8**).* TMEDA (0.30 mL, 2 mmol) was added via a syringe to a suspension of NaBr (150 mg, 1 mmol) in *n*-hexane (10 mL), and the reaction mixture was stirred for 24 h. NaHMDS prepared in situ [*n*-butylsodium (240 mg, 3 mmol) in *n*-hexane (10 mL) and bis(trimethylsilyl)amine (0.63 mL, 3 mmol)] was added via a cannula to the NaBr/TMEDA reaction mixture to give a white suspension, which was stirred for 5 days. The solvent was removed under vacuum until dryness, and toluene (30 mL) was added. The reaction was heated with a heat gun, and the hot reaction mixture was filtered to give a yellow solution. The solvent was partially removed under vacuum (4 mL), and the solution was placed at −33 °C (24 h) to yield **8** as colorless crystals suitable for an X-ray diffraction study. **8** was filtered, washed with cool *n*-hexane (10 mL), and dried under vacuum for 30 min. Yield: 470 mg, 0.55 mmol, 55%. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K): δ 0.35 (s, 27 H, Me_3Si), 1.84 (s, 4 H, CH_2, TMEDA), 2.00 (s, 12 H, Me, TMEDA). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6, 300 K): δ 7.2 (Me_3Si), 46.2 (Me, TMEDA), 57.2 (CH_2, TMEDA). Anal. Calcd (found) for $C_{30}H_{86}BrN_7Na_4Si_6$: C, 40.70 (40.71); H, 9.79 (9.65); N, 11.07 (10.99).

Crystallographic Analysis. Crystallographic data were recorded at 123(2) K on Oxford Diffraction Xcalibur and Gemini diffractometers with Mo Kα (λ = 0.71073 Å, for **1**−**5**) and Cu Kα (λ = 1.5418 Å, for **6**−**8**) radiation, respectively. Structures were refined to convergence on F^2 and against all independent reflections by full-matrix least squares using *SHELXL-2013* programs.[36] The I atom in **4**, two TMDAE ligands in **5**, one TMEDA ligand in **7**, and three HMDS and one TMEDA ligand in **8** were modeled as disordered over two sites. The geometries of the disordered groups were restrained to approximate typical values. The *SQUEEZE* routine of *PLATON*[37] was used in the structure of **5** to remove the effects of disordered solvent molecules. Approximately the equivalent of 272 electrons were removed from approximately 2210 Å^3 of the "void" cell space. This approximated to five to six molecules of *n*-hexane per unit cell. Selected crystallographic parameters are given in Tables S1 and S2, and full details are given in the deposited CIF files (CCDC 1411192−1411198 for **1**, **2**, and **4**−**8** respectively). These data in CIF format can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01584.

Crystallographic data for complexes **1**, **2**, and **4**−**8** in CIF format (CIF)

Crystallographic and refinement data, ^{1}H and ^{13}C NMR spectra for complexes **1**−**8**, and ^{133}Cs NMR spectroscopic data for [(Me_6TREN)Cs(HMDS)] (PDF)

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Notes

The authors declare no competing financial interest.

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