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# A Structural and Computational Study of Synthetically Important Alkali-Metal/Tetramethylpiperidide (TMP) Amine Solvates

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**Abstract:** Two heavy alkali-metal salts of the sterically demanding amine, 2,2,6,6-tetramethylpiperidine (TMPH), have been prepared using different methodologies. Complex **1**, [{(tmeda)Na(tmp)}$_2$] (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), can be synthesized by a deprotonative route. This is achieved by reacting butylsodium with TMPH in the presence of excess TMEDA in hexane. The potassium congener [{(tmeda)K(tmp)}$_2$] (**2**), can be prepared by treating KTMP (made using a metathesis reaction between LiTMP and potassium *tert*-butoxide) with an excess of TMEDA in hexane. In the solid state, **1** and **2** are essentially isostructural. They are discretely dimeric and their framework consists of a four-membered M-N-M-N ring (M = Na or K, N = TMP). Due to the high steric demand of the TMP ligand, the TMEDA molecules bind to the metal centers in an asymmetric manner. In **2**, each of the coordination spheres of the metals is completed by an agostic K···CH$_3$(TMP) interaction. DFT calculations at the B3LYP/6-311G$^{**}$ level give an insight into why **1** and **2** adopt dramatically different structures from their previously reported, "open-dimeric", lithium counterpart. The theoretical work also focuses on the TMEDA-free parent amide complexes and reveals that the energy difference for the formation of [{M(tmp)}$_x$] (in which, M = Li or Na, $x = 3$ or 4; and M = K, $x = 2$, 3 or 4) are small.

**Keywords:** alkali metals · amides · coordination chemistry · density functional calculations · structure elucidation

## Introduction

From a synthetic chemist's standpoint, alkali-metal (especially lithium) amide complexes are amongst the most useful and commonly encountered organometallic reagents. In particular, the alkali-metal salts of hexamethyldisilazane (HMDS(H)),[1–6] diisopropylamine (DA(H)),[7–10] and 2,2,6,6-tetramethylpiperidine (TMP(H))[11] are prevalent in many synthetic chemistry laboratories. These reagents are often considered bastions of synthetic chemistry for several reasons. Firstly, and most importantly, they have a high Brønsted basicity, but are generally weakly nucleophilic in nature. The amides also exhibit a higher basicity than their alkoxide counterparts, are employed to induce kinetic deprotonations, are often hydrocarbon (or THF) soluble, are safer to handle than alkali metal hydrides and alkyls, and are commercially available. There are numerous accounts of alkali-metal amides being used to achieve alkali-metal/hydrogen exchange, and the use of alkali-metal amides (in particular those of lithium) has been well reviewed.[8,12–15] More specifically, the amides have been used recently in certain transformations such as the generation of enolates,[16–25] condensation and ring-formation processes,[26–28] directed *ortho*-metalations (D*o*M),[29–39] rearrangement and isomerization processes,[40–44] and in Wittig reactions.[45–48]

From a structural perspective, the chemistry of the alkali metal amides has been the focus of a great deal of attention, both in solution and in the solid state. Collum and co-workers have painstakingly studied the solution behavior of various lithium amides in both nonpolar and polar solvents.[49–51] With particular relevance to this study, the aforementioned group have determined previously (using $^6$Li and $^{15}$N NMR spectra) the hydrocarbon solution structures of LiTMP and LiPMP (where PMP = 2,2,4,6,6-pentamethylpiperidide). They found that the solutions consisted of a mixture of a cyclic trimer and four distinct cyclic tetramers (each with a different symmetry: $C_{4h}$, $D_{2h}$, $C_{2v}$, and $C_s$).[52] Three years

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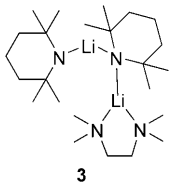
later they described the solution behavior of LiTMP and its "surrogate" LiPMP in the presence of the common donor solvent *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA).[53] Their findings indicated that, as expected, deaggregation of the trimer/tetramers occurred. Intriguingly, the expected solvated cyclic dimer could not be detected; instead, a monomeric and an "open-dimeric" species were identified.

A fascinating array of solid-state structures is possible by slightly modifying the electronic and steric properties of the amido ligand. For instance, in the absence of donor solvent, dimers,[54–60] trimers,[61–66] tetramers,[67,68] hexamers,[69] and polymers[70] of lithium secondary amides can be isolated. As expected the introduction of a donor solvent generally decreases the aggregation state to form smaller aggregates.[71,72] Most pertinent to this study are the alkali-metal salts of TMP(H). The solid-state structures of donor-free cyclic oligomers $[\{Li(tmp)\}_4]$[68] and $[\{Na(tmp)\}_3]$[73] have been reported. Counterintuitively, the Li amide has a higher state of oligomerization than its Na counterpart. Williard et al. have published the synthesis and structure of the TMEDA hemisolvated complex $[(tmeda)\{Li(tmp)\}_2]$[74] **3** (Figure 1).



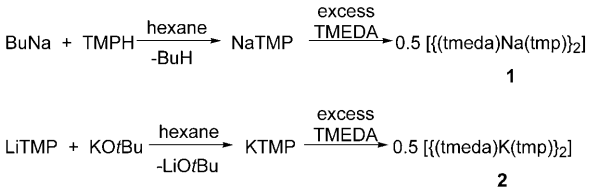
**3**

Figure 1. Structural formula of $[(tmeda)\{Li(tmp)\}_2]$[74] (**3**), highlighting its open-dimeric structural motif.

Surprisingly, considering the wide-reaching appeal of these reagents and their extensive synthetic utilization in polar (e.g., ethereal) solvents, this structure hitherto represents the only donor complex of a homometallic alkali-metal tetramethylpiperidide. The structure is described as an "open dimer" (c.f., solution-state studies[53]), in which there are two chemically unique Li atoms: one is formally two-coordinate, bridging between two TMP anions; the other is three-coordinate and is bound to one TMP anion and two N atoms of a terminal TMEDA ligand. From these solid-state data, the authors were able to rationalize a key step in the reaction pathway of the aldol reaction. Over the past few years we have shown that heterobimetallic alkali-metal/divalent-metal TMP-containing complexes (such as the zincate $[(tmeda)NaZn(t\mathrm{Bu})_2(tmp)]$)[75] can induce a special synergic chemistry culminating in the regioselective alkali-metal-mediated magnesiation/zincation of arenes[76–83] and metallocenes[84–89] and opening up the concept of inverse crown chemistry.[90,91] To build up a full understanding of the chemistry of the mixed metal systems, for example, the aforementioned Na–Zn system,[75] we have decided to turn our attention to the TMEDA complexes of the component alkali-metal amide reagents. Thus, herein we report the synthesis, solid- and solution-state structures of two new TMEDA-solvated heavy-alkali-metal TMP complexes, $[\{(tmeda)M(tmp)\}_2]$ (in which M = Na or K). We also detail a series of DFT calculations used to examine the unusual coordination chemistry of the $[(tmeda)_x\{M(tmp)\}_y]$ systems (in which M = Li, Na, and K).

## Results and Discussion

**Syntheses**: Scheme 1 outlines the synthesis of amides **1** and **2**. Sodium amide **1** was made by direct sodiation of the amine TMPH with an equimolar amount of freshly prepared




Scheme 1. The preparation of TMEDA-solvated alkali metal tetramethylpiperidides **1** and **2**.

BuNa[92] in hexane. After stirring for two hours, TMEDA was introduced to the cream-colored suspension. An excess (three molar equivalents) was required to produce a homogeneous solution. Cooling this yellow solution to −27 °C yielded a crop of colorless needlelike crystals. The crystals were found to be highly soluble in the mother solution, therefore the isolated yield was only moderate (21 %). Amide **1** was also prepared directly (confirmed by NMR spectroscopy) by adding an excess of TMEDA to freshly prepared and isolated NaTMP. Potassium amide **2** was synthesized by using a slightly altered methodology. Freshly prepared LiTMP was treated with an equimolar quantity of potassium *tert*-butoxide in a metathesis reaction. The resultant potassium amide was isolated from the reaction mixture, before being suspended in hexane and treated with an excess (four molar equivalents) of TMEDA to produce a red solution. This solution was cooled to −27 °C to aid crystallization. Red crystals of **2** were deposited and, as for **1**, were found to be extremely soluble in hexane.

**Solid-state structures**: The molecular structures of **1** and **2** were determined by X-ray diffraction studies and are shown in Figures 2 and 3, respectively (accompanied, in the case of Figure 3, by the appropriate key bond lengths and angles). Both **1** and **2** are closed dimers in the solid state in comparison to the open-dimeric lithium congener **3**. Unfortunately, the structure of **1** contains two sites of disorder: one at a TMP ligand (N(6)) and the other at the TMEDA ligand attached to Na(2). This disorder arises from the ligands in question adopting two unique conformations, and prohibits an in-depth discussion of the geometric parameters of **1**. The dimeric framework of **1** consists of a Na-N-Na-N ring and the coordination spheres of the Na atoms appear to resemble those found in its diisopropylamide analogue $[\{(tmeda)Na(da)\}_2]$ **4**.[93] The non-disordered TMP unit adopts a chair conformation.

Turning to the molecular structure of **2**, this can be discussed in more detail as it contains no disorder features. The dimeric framework of **2** consists of a planar (sum of endocyclic angles, 359.99°) $K_2N_2$ ring, in which the M−N bonds

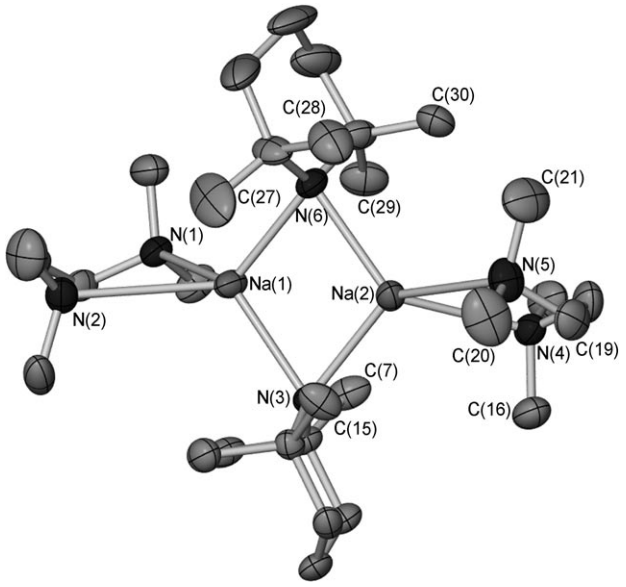



Figure 2. The molecular structure of **1**. Key structural parameters are not included due to the disorder components associated with: 1) TMEDA molecule attached to Na(2); and 2) TMP ligand which contains N(6).

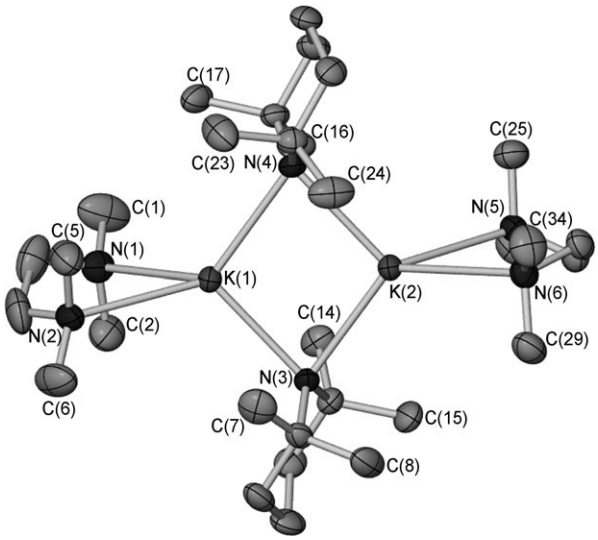



Figure 3. The molecular structure of **2**. For clarity, all H atoms and K···C contacts have been omitted (see Figure 4). Thermal ellipsoids are shown at 50% probability level. Selected bond lengths [Å] and angles [°]: K(1)–N(1), 2.934(2); K(1)–N(2), 2.948(2); K(1)–N(3), 2.744(2); K(1)–N(4), 2.836(2); K(2)–N(3), 2.825(2); K(2)–N(4), 2.764(2); K(2)–N(5), 2.882(2); K(2)–N(6), 3.039(2); K(1)···C(7), 3.215(2); K(2)···C(24) 3.159(3); N(1)-K(1)-N(2), 61.83(5); N(1)-K(1)-N(3), 119.86(5); N(1)-K(1)-N(4), 122.20(4); N(2)-K(1)-N(3), 119.44(4); N(2)-K(1)-N(4), 129.70(5); N(3)-K(1)-N(4), 101.41(4); N(3)-K(2)-N(4), 101.20(4); N(3)-K(2)-N(5), 124.17(4); N(3)-K(2)-N(6), 126.55(4); N(4)-K(2)-N(5), 116.66(4); N(4)-K(2)-N(6), 123.64(4); N(5)-K(2)-N(6), 62.09(4); K(1)-N(3)-K(2), 78.95(4); K(1)-N(4)-K(2), 78.43(4).

vary considerably within the ring (range, 2.744(2)–2.836(2) Å; i.e., a difference of 0.092 Å). The two shortest distances (K(1)–N(3) and K(2)–N(4)) represent the metal–anion σ interactions, while the longer distances (K(1)–N(4) and K(2)–N(3)) describe the metal–N lone-pair dative interactions. The coordination spheres of the two K centers are completed by binding of the TMEDA molecules and a series of agostic K···C(H) interactions. The extreme steric bulk of the TMP ligand appears to affect the bonding mode of the TMEDA ligands to the K centers. Focusing on K(1), the K–$N_{TMEDA}$ bond lengths indicate that the diamine is bonding in a bidentate fashion (K(1)–N(1) and K(1)–N(2) distances are 2.934(2) and 2.948(2) Å, respectively). The potassium atom K(1) is also bound to two TMP–N centers, and is further stabilized by a short K···C agostic interaction (K(1)···C(7) distance, 3.215(2) Å) to a methyl C atom of TMP (C(7); (Figure 4). The coordination sphere of K(2) differs appreciably from that of K(1). Thus, the TMEDA mole-

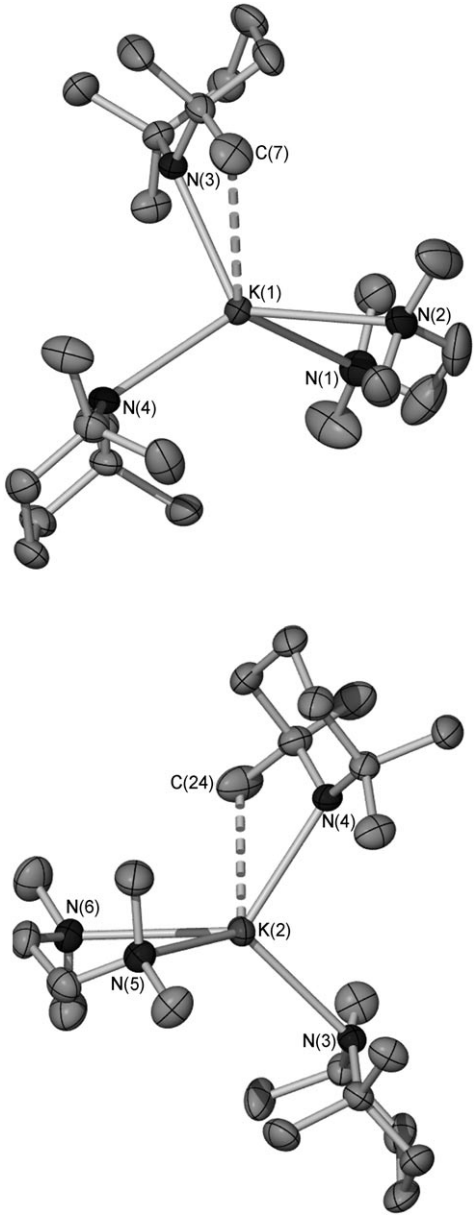



Figure 4. The coordination environments of K(1) and K(2) in **2** highlighting the intramolecular agostic interactions (dashed bonds).

cule is appended to K(2) rather more asymmetrically (K(2)−N(5) and K(2)−N(6) distances are 2.882(2) and 3.039(2) Å respectively). Again, the metal center is stabilized by an agostic interaction (K(2)···C(24) distance, 3.159(2) Å, Figure 4). Although rare, there is a precedent for TMEDA bonding to an alkali metal in a monodentate manner. Some particularly relevant examples include $[\{(tmeda)Li(da)\}_\infty]$,[94] $[\{(tmeda)Li(dmp)\}_\infty]$[95] in which DMP = 2,6-dimethylpiperidide, and the potassium iminophosphoranylenamide, $[\{(tmeda)K\{N(H)C(Ph)C(H)P(Ph)_2{=}NSiMe_3\}\}_2]$.[96] The coordination environments of the K atoms in **2** can be compared to those found in the diisopropylamide analogue $[\{(tmeda)K(da)\}_2]$ (**5**).[97] Complex **5** is centrosymmetric, hence the TMEDA molecules are crystallographically equivalent. In this case, the two $K{-}N_{TMEDA}$ bonds are almost identical in length (mean distance, 2.886 Å). The agostic interactions in **5** are somewhat longer than those found in **2** (shortest K···C distances in **5** are 3.375(3) and 3.384(3) Å).

**Solution structures**: Crystalline samples of **1** and **2** are soluble in $C_6D_6$, hence they were subjected to an NMR spectroscopic study in this solvent. Due to the highly air/moisture-sensitive nature of these compounds, resonances pertaining to traces of the parent amine, TMPH, were consistently observed in the spectra, even though the NMR solvent was subjected to a seemingly rigorous drying/degassing regime. The $^1$H NMR spectra of **1** and **2** (see Supporting Information) reveal that resonances associated with the TMP and TMEDA ligands are observed. Focusing on **1**, the chemical shifts due to the TMP anion (Table 1) are significantly deshielded (by 0.37, 0.41, and 0.60 ppm for the C*H*$_3$, β-C*H*$_2$ and γ-C*H*$_2$ H atoms, respectively) from their counterparts in the parent amine. Additionally, the chemical shifts for **1** are also more deshielded than the respective H atoms in the donor-free sodium amide, NaTMP (Table 1).

Table 1. $^1$H NMR data for several TMP-containing species. All experiments were conducted at 300 K in $C_6D_6$.

| | C*H*$_3$ (TMP) | β-C*H*$_2$ (TMP) | γ-C*H*$_2$ (TMP) | C*H*$_3$ (TMEDA) | C*H*$_2$ (TMEDA) |
|---|---|---|---|---|---|
| TMPH | 1.06 | 1.22 | 1.53 | – | – |
| TMEDA | – | – | – | 2.12 | 2.36 |
| NaTMP | 1.11 | 1.36 | 1.89 | – | – |
| **1** | 1.43 | 1.63 | 2.13 | 1.92 | 1.90 |
| KTMP | 1.23 | 1.40 | 1.93 | – | – |
| **2** | 1.32 | 1.54 | 2.05 | 1.94 | 2.01 |
| LiTMP | 1.36 | 1.37 | 1.78 | – | – |
| **3** | 1.36/1.47 | 1.37/1.54 | 1.78/2.05 | 1.95 | 1.87 |

Only two broad resonances, indicative of a dynamic process, can be attributed to TMEDA, suggesting that the asymmetrical solid-state structure is not maintained in solution, but these differ significantly from uncoordinated TMEDA, indicating that it is ligating to the metal center at least part of the time. Interestingly, the $^{13}$C NMR spectra show that there is not a great deal of differentiation between **1**, **2**, **3**, and their parent TMEDA-free complexes (Table 2).

Table 2. $^{13}$C NMR data for several TMP-containing species. All experiments were conducted at 300 K in $C_6D_6$.

| | α-*C* (TMP) | *C*H$_3$ (TMP) | β-*C*H$_2$ (TMP) | γ-*C*H$_2$ (TMP) | *C*H$_3$ (TMEDA) | *C*H$_2$ (TMEDA) |
|---|---|---|---|---|---|---|
| TMPH | 49.5 | 32.0 | 38.6 | 18.8 | – | – |
| TMEDA | – | – | – | – | 46.0 | 58.4 |
| NaTMP | 52.3 | 38.2 | 42.4 | 20.8 | – | – |
| **1** | 52.8 | 37.7 | 42.6 | 21.5 | 46.2 | 57.6 |
| KTMP | 52.5 | 37.0 | 42.8 | 20.8 | | |
| **2** | 52.7 | 37.0 | 42.7 | 21.3 | 45.7 | 57.6 |
| LiTMP | 52.4 | 37.0 | 42.8 | 20.1 | – | – |
| | 52.3 | 37.1 | 43.2 | 19.9 | | |
| **3** | 52.4 | 37.0 | 42.8 | 20.1 | 45.8 | 56.8 |
| | 52.3 | 36.6 | 42.8 | 21.1 | | |

In keeping with its Na analogue, the $^1$H NMR spectrum of **2** reveals that the TMP signals are shifted downfield when compared with base-free KTMP and TMPH (Table 1). However, the effect is much less pronounced than it is for the Na amides. As with **1**, the TMEDA shifts are far removed from those of the unligated diamine.

The solution structure of the open-dimeric lithium amide **3** was also obtained for comparison. Complex **3** was prepared using Williard's methodology.[74] The crystals were dissolved in $C_6D_6$ and subjected to an NMR spectroscopic study. Unlike the other amide complexes studied herein, the $^1$H NMR spectrum revealed that there were two distinct sets of TMP resonances present, a scenario which would be expected if the solid-state structure remained intact in solution (i.e., bridging and terminal ligands). However, as previously alluded to by Collum et al.,[53] the chemical shifts presented in Table 1 appear to suggest that on dissolution, the open dimer is cleaved to give donor-free LiTMP (Table 1) and monomeric [(tmeda)Li(tmp)].

**Calculations**: A series of calculations using the Gaussian 03 package[98] was performed to enhance our understanding of three key areas in this study. For each species, geometry optimization was undertaken at the HF/6-31G*[99] level, followed by a frequency analysis. Then the geometry was refined by further calculation at the B3LYP[100]/6-311G**[101] level. The structural parameters reported were taken from the DFT calculations, while the total energy abstracted from the DFT calculation was adjusted by inclusion of the zero-point energy value from the HF calculation modified by the factor 0.91. Firstly, the structures of donor-free alkali-metal tetramethylpiperidides were examined to unravel the apparent anomalies in the solid-state structures obtained for LiTMP and NaTMP (recall that the former is tetrameric; whilst the latter is trimeric). Secondly, the effect of introducing TMEDA into the reactions was studied to provide an insight into the reasons why such different solid-state structures exist for the TMEDA solvates of M(TMP) (M = Li,

Na, or K). Figure 5 shows the relevant models which were considered during this study. Tables 3–8 contain the geometric and thermodynamic data which were obtained during the course of this study.

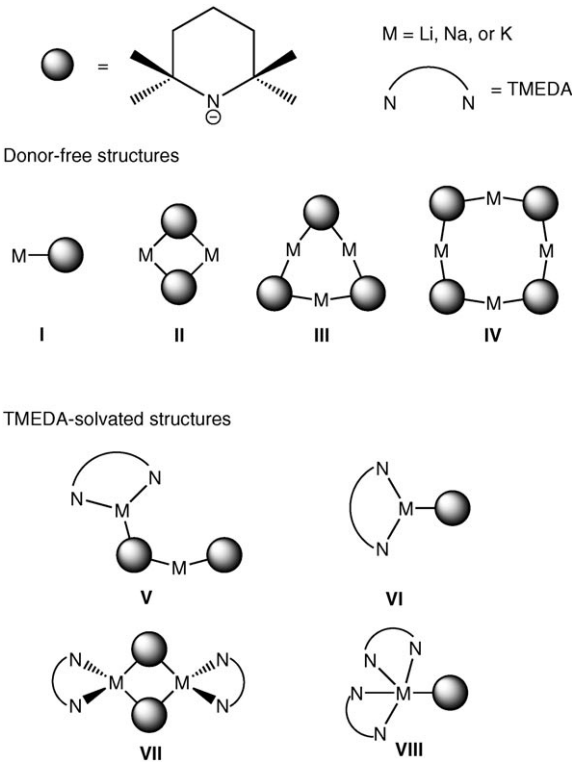



Figure 5. Diagrammatic representation of the models which were studied with DFT calculations.

As discussed earlier, the solid-state structures of donor-free LiTMP[68] and NaTMP[73] were unveiled a few years ago. Unfortunately, no solid-state characterization of the K analogue has been thus far forthcoming, presumably due to the low solubility of the complex in common hydrocarbon and arene solvents, which renders its crystallization difficult. To corroborate the solid-state information at hand, various donor-free structures of LiTMP and NaTMP were modeled, as well as those for KTMP, to give a possible insight into the solid-state structure of this species. In our investigation into the structures of the tetramers [{M(tmp)}$_4$], it was thought useful to look at the four distinct geometries of the cyclic tetramers as proposed by Collum[57], namely the $C_{4h}$, $D_{2h}$, $C_{2v}$, and $C_s$ model isomers (Figure 6). The last three models are constructed from the first structure by: 1) rotating two *trans* TMP groups by 180° to give the $D_{2h}$ model, 2) rotating two *cis* TMP groups by 180° to give the $C_{2v}$ model, and 3) rotating one of the TMP groups 180° to give the $C_s$ model (Figure 5). No geometric constraints were imposed during the optimization procedure. It was found that for these three models, no plane of symmetry was found after the optimization procedure was undertaken, that is, rotation of the TMP group(s) caused a twisting of the (M–N)$_4$ backbone of

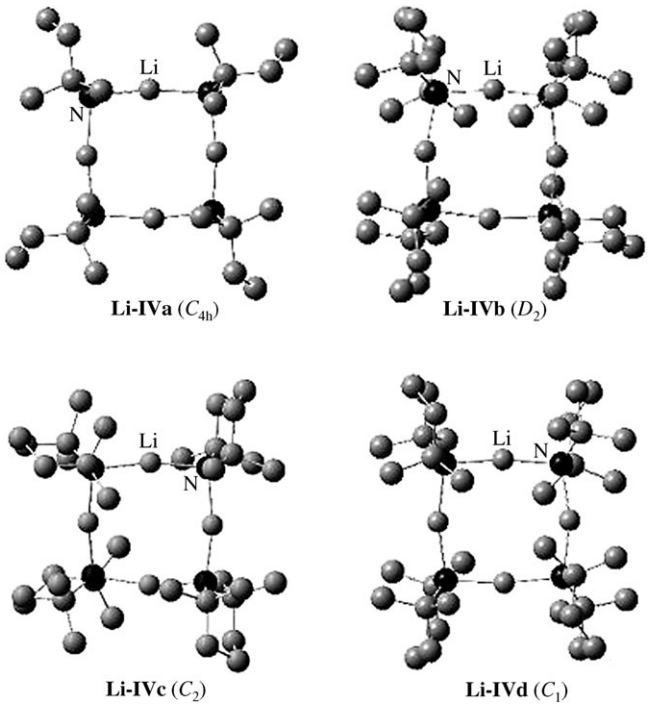



Figure 6. Four isomeric models of (Li–TMP)$_4$ and their respective symmetries. For brevity, only the Li examples are shown. The models for the Na and K analogues can be found in the Supporting Information.

the molecules due to steric interference of the methyl constituents. The resulting symmetry of the models was reduced ($D_{2h}\rightarrow D_2$, $C_{2v}\rightarrow C_2$, and $C_s\rightarrow C_1$). However, the plane of symmetry was found to be retained for the $C_{4h}$ model. The resulting total energies and relative energies are given in Table 3.

Table 3. Resulting total and relative energies of the [{M(tmp)$_4$}] models **M-IVa**–**M-IVd**.

| | Resulting total energy [a.u.] | Relative energy [kcal mol$^{-1}$] |
|---|---|---|
| **Li-IVa** ($C_{4h}$) | −1663.928923 | 0.0 |
| **Li-IVb** ($D_2$) | −1663.928138 | +0.49 |
| **Li-IVc** ($C_2$) | −1663.928407 | +0.32 |
| **Li-IVd** ($C_1$) | −1663.927514 | +0.88 |
| **Na-IVa** ($C_{4h}$) | −2282.966120 | +0.14 |
| **Na-IVb** ($D_2$) | −2282.966231 | +0.07 |
| **Na-IVc** ($C_2$) | −2282.966340 | 0.0 |
| **Na-IVd** ($C_1$) | −2282.966304 | +0.02 |
| **K-IVa** ($C_{4h}$) | −4033.474196 | +1.25 |
| **K-IVb** ($D_2$) | −4033.476194 | 0.0 |
| **K-IVc** ($C_2$) | −4033.475859 | +0.21 |
| **K-IVd** ($C_1$) | −4033.476081 | +0.07 |

It can be seen that there is very little difference in energy between the four structural models for each of the tetrameric species. It is thus not possible from this level of calculation to categorically predict the correct structure of the three alkali metal tetramers studied. This is in pleasing

agreement with the findings of Collum regarding the possible structures of $(LiTMP)_4$ in solution.[57] On descending Group 1 from Li→K it is clear that the models containing rotated TMP groups become relatively more stable, presumably due to the longer M–N bond lengths allowing the steric influences to be minimized. Due to the similar thermodynamic stabilities and indeed key structural dimensions of the respective models **M-IVa**–**M-IVd** only those relating to **M-IVa** need be discussed here in full detail. All other experimental data collected during our study can be found in the Supporting Information.

Two models were invoked for the dimeric species. The **M-IIa** models have $C_2$ symmetry while **M-IIb** structures have *Ci* symmetry. It was found that the **M-IIa** model was consistently more stable than the **M-IIb** isomers although the energy difference decreased as M changed from M = Li (3.96 kcal mol$^{-1}$) to Na (0.37 kcal mol$^{-1}$) and to K (0.07 kcal mol$^{-1}$). For the even heavier alkali metal species, it is envisaged that the stable geometry will have $C_{2h}$ symmetry.

For each of the **M-III** species, two models were chosen following the ideas of Collum et al.[52] Model **M-IIIa** is the classical $D_{3h}$ structure as found in the crystal structure of $[\{Na(tmp)_3\}]$,[73] while **M-IIIb** has one of the TMP ligands present in **M-IIIa** rotated by 180°. The calculations revealed that **M-IIIa** is more stable than **M-IIIb** by 1.43, 0.93, and 0.33 kcal mol$^{-1}$ for M = Li, Na, and K, respectively. The energy difference between the two models narrows as the alkali metal increases in size. This may be attributed to the fact that the M–N bond lengths are increased, hence the accompanying extra steric repulsion generated by the rotation of a TMP group is minimized.

As expected, the monomeric models (**M-I**) are all unstable with respect to their higher oligomers (Table 4, entries 1–4). For the Li and Na amides, the trimers (**Li-IIIa** and **Na-IIIa**) are significantly more stable than their respective dimeric oligomers **Li-IIa** and **Na-IIa** (by −4.10 and −5.25 kcal mol$^{-1}$, respectively). The most striking result from this set of data is that the energy difference between respective trimeric and tetrameric (**Li-IVa** and **Na-IVa**) species is minute (+0.04 and −0.11 kcal mol$^{-1}$ for Li and Na, respectively). No definite conclusions can be drawn with such small $\Delta E$ differences given that the calculations do not take into account crystal packing forces, nor do they take into account solvent effects, which have a significant bearing on the entropy of such systems. Experimentally, there is a precedent for the existence of more than a single oligomeric form (i.e., polymorphic forms) of alkali-metal amides. For instance, the chain structure of polymeric sodium bis(trimethylsilyl)amide (NaHMDS) was published by Atwood.[102] Two decades later, Nöth[103] and Dreiss[104] independently reported its trimeric variant.

Table 4. Relative energies from TMEDA-free calculations.

| | | $\Delta E$ [kcal mol$^{-1}$] |
|---|---|---|
| 1 | **Li-I**→1/2 **Li-IIa** | −20.52 |
| 2 | **Li-I**→1/3 **Li-IIIa** | −24.62 |
| 3 | **Li-I**→1/4 **Li-IVa** | −24.58 |
| 4 | **Na-I**→1/2 **Na-IIa** | −19.30 |
| 5 | **Na-I**→1/3 **Na-IIIa** | −24.55 |
| 6 | **Na-I**→1/4 **Na-IVc** | −24.70 |
| 7 | **K-I**→1/2 **K-IIa** | −15.16 |
| 8 | **K-I**→1/3 **K-IIIa** | −16.63 |
| 9 | **K-I**→1/4 **K-IVb** | −16.31 |

Returning to our theoretical studies, model **K-IIIa** appears to be the most stable potassium oligomer (Table 4, entry 8), although the energy difference for the association (from **K-I**) of **K-IIa** and **K-IIIa**/**K-IVb** is much less pronounced than that for the Li and Na models. This implies that the solid-state structure of KTMP, could it be determined, is as likely to be dimeric as it is trimeric or tetrameric. Although this train of thought appears to be at odds with convention, alkali-metal HMDS structures may provide evidence that would appear to support the above theoretical data. In the crystal, LiHMDS is trimeric,[105] whilst NaHMDS is known to be polymeric and trimeric (vide infra). KHMDS is composed of $(K–N)_2$ dimeric units, which, through intermolecular agostic interactions, extend to give a polymeric supramolecular structure.[106] A possible explanation for the stability of the dimeric $(K–N)_2$ units may arise from the steric demands of the ligand. For example, in all of the models/crystal structures discussed thus far, the metal is two coordinate with respect to N atoms. In model **Li-IIa**, the distance between the two N centers of the amido ligands is only 3.289 Å. These N centers are highly charged and may be subject to intramolecular repulsion. If the distance between the N atoms is increased (with subsequent narrowing of the Li-N-Li angle) then repulsion between the metal cations may result. Therefore, sterically the lithium amide is more stable if it adopts a structure in which there is a greater distance between two N (and indeed Li) atoms (e.g., dimensions for **Li-IVa**: Li···Li distances, 3.103 and 4.388 Å, respectively, for adjacent and transannular Li atoms; and N···N distances, 4.041 and 5.716 Å for adjacent and transannular N atoms, respectively). For the significantly larger potassium cation, the K–N bonds are of a sufficient length to accommodate a dimeric structure without any significant loss in stability (K···K and N···N distances in **K-IIa**, 3.477 and 4.265 Å, respectively). Parallel with the situation for KHMDS, both RbHMDS and CsHMDS are known to be dimeric in the solid state.[107] Focusing on the structural parameters of **K-IIa**, there are two distinct K–N bond lengths. These may be designated as the strong σ-bond between the K atom and the anionic N center (2.693 Å), and the weaker K–N dative interaction (2.809 Å). This scenario is similar to, although more pronounced than that observed for $[\{K(hmds)\}_2]$ (K–N distances, 2.745(3) and 2.801(3) Å).

Returning to the lithium models, the mean Li–N bond in **Li-IVa** (2.029 Å) compares favorably with the respective bond in the solid-state structure **3** (mean, 2.00 Å) (Table 5). Also the Li-N-Li and N-Li-N bond angles in **Li-IVa** (99.8° and 170.2°, respectively) are again in close agreement with those in the crystal structure (mean, 101.55° and 168.5°).

Table 5. Key calculated structural parameters for "donor-free" **M-I**–**M-IVa** and experimentally determined parameters for "donor-free" LiTMP and NaTMP.

| | M = Li | M = Na | M = K |
|---|---|---|---|
| **M-I** parameters | | | |
| M–N [Å] | 1.764 | 2.138 | 2.444 |
| N–$C_\alpha$ [Å] | 1.463 | 1.457 | 1.456 |
| M···C(Me) [Å] | 2.793 | 3.011 | 3.235 |
| **M-II** parameters | | | |
| M–N [Å] | 1.956, 1.989 | 2.338, 2.403 | 2.693, 2.809 |
| N···N [Å] | 3.289 | 3.838 | 4.265 |
| M···M [Å] | 2.178 | 2.782 | 3.477 |
| N-M-N [°] | 112.9 | 108.1 | 101.6 |
| M-N-M [°] | 67.0 | 71.8 | 78.4 |
| **M-III** parameters | | | |
| M–N [Å] | 1.991, 2.045 | 2.337, 2.372 | 2.747, 2.756 |
| N···N [Å] | 3.913 | 4.510 | 5.151 |
| M···M [Å] | 2.813 | 3.429 | 4.252 |
| N-M-N [°] | 151.7 | 146.5 | 138.8 |
| M-N-M [°] | 88.3 | 93.5 | 101.2 |
| **M-IVa** parameters | | | |
| M–N [Å] | 2.014, 2.043 | 2.352, 2.358 | 2.761, 2.771 |
| N···N [Å] | 4.041, 5.716 | 4.676, 6.613 | 5.455, 7.714 |
| M···M [Å] | 3.103, 4.388 | 3.699, 5.230 | 4.506, 6.373 |
| N-M-N [°] | 170.2 | 166.5 | 160.9 |
| M-N-M [°] | 99.8 | 103.5 | 109.1 |
| X-ray data | [{Li(tmp)}$_4$] | [{Na(tmp)}$_3$] | |
| M–N [Å] | 2.014(2), 2.018(2), 1.977(2), 1.989(2) | 2.362(2), 2.307(2) | |
| N-M-N [°] | 168.2(4), 168.8(4) | 143.76(6) | |
| M-N-M [°] | 101.6(3), 101.5(3) | 96.24(6) | |

The key structural parameters of **Na-IIIa** (mean values: Na–N, 2.345 Å; N-Na-N, 146.5°; and Na-N-Na, 93.5°) are also in accord with the crystallographically-determined data (mean values: Na–N, 2.335 Å; N-Na-N, 143.8°; and Na-N-Na, 96.2°).

To give an added insight into the X-ray data presented in this article, a series of TMEDA-solvated molecules were modeled (**M-V**–**VIII**) (Figure 5). As alluded to earlier, the only structurally characterized TMEDA solvate (actually a hemisolvate) of LiTMP exists as an open dimer. In addition to studying the equivalent DFT model (**Li-V**), other plausible structural motifs were investigated. Model **Li-VII** represents a "conventional" TMEDA-solvated closed dimer. The calculations revealed that the geometry optimization for this species could not be achieved due to the TMEDA preferring to bond only through one of the $NMe_2$ units. This information suggests that sterically, a four-coordinate Li center is not feasible in such a system, hence the need for an open-dimeric arrangement (i.e., **Li-V**). The Li centers in **Li-V** and in Williard's crystal structure of the same compound are two or three coordinate.[74]

This can be compared with the scenario for the aforementioned TMEDA-free species in which the alkali metal is consistently two coordinate. The formation of the open-dimeric species **Li-V**, through the combination of two molecules of **Li-I** and one molecule of TMEDA (Table 6, entry 1), is highly exothermic (−51.53 kcal mol$^{-1}$). The key geometric parameters calculated for **Li-VII** are in very good agreement with those for Williard's X-ray data: all the Li–N bond distances and important angles are found to be within experimental error (Table 7).[74]

Table 6. Relative energies from the "open-dimer" calculations.

| | | $\Delta E$ [kcal mol$^{-1}$] |
|---|---|---|
| 1 | 2 **Li-I** + TMEDA → **Li-V** | −51.53 |
| 2 | **Li-IIa** + TMEDA → **Li-V** | −14.44 |
| 3 | 1/2 **Li-IVa** + TMEDA → **Li-V** | −2.36 |
| 4 | **Li-V** + TMEDA → **Li-VII** | +5.16 |
| 5 | 2 **Na-I** + TMEDA → **Na-V** | −47.67 |
| 6 | **Na-IIa** + TMEDA → **Na-V** | −9.08 |
| 7 | 2/3 **Na-IIIa** + TMEDA → **Na-V** | +1.42 |
| 8 | **Na-V** + TMEDA → **Na-VII** | −7.29 |

Turning to the TMEDA derivatives of NaTMP, energetically, the formation of **Na-V** from two molecules of **Na-I** and one molecule of TMEDA was found to be highly exothermic (−47.67 kcal mol$^{-1}$; Table 6, entry 5). On the other hand, the solvation of trimeric NaTMP (**Na-III**) by TMEDA to produce **Na-V** was modestly endothermic (+1.42 kcal mol$^{-1}$; Table 6, entry 7), implying that the formation of an open-dimer arrangement is not thermodynamically favored.

As expected, the solvation of the one-coordinate Na atom in **Na-I** (by TMEDA) is exothermic ($\Delta H$, −22.60 kcal mol$^{-1}$; Table 8, entry 7). Dimerization of **Na-VI** (to form **Na-VII**) is also exothermic (−4.91 kcal mol$^{-1}$; Table 8, entry 8). To reiterate, in the solid state, NaTMP is known to be trimeric (i.e., akin to **Na-III**). With respect to **Na-III**, it was discovered that the formation of monomeric **Na-VI** was thermodynamically unfavored (+2.0 kcal mol$^{-1}$, see later), whilst the formation of dimeric **Na-VII** was favored (−2.9 kcal mol$^{-1}$). This data supports the X-ray study for **1** that was detailed earlier. Structurally, due to the disorder which was present in the X-ray data for **1**, a meaningful comparison between the observed data and calculated data could not be made.

The TMEDA solvates of KTMP were also studied. The calculations, in the main, mirror the results obtained using the sodium models. However, some notable differences were observed. For instance, the coordination of TMEDA to monomeric **M-I** was considerably more exothermic (by −8.63 kcal mol$^{-1}$) for sodium than for potassium (Table 8, entries 7 and 15, respectively). Counter to this scenario, the dimerization of **M-VI** (to give **M-VII**) was more exothermic (by −6.37 kcal mol$^{-1}$) for the potassium amide (Table 8, entries 8 and 16). In keeping with the increased size of the cation, the energy gained from the dissociation of trimeric **K-III** by using two TMEDA molecules is greater (by −5.92 kcal mol$^{-1}$) than for that associated with its Na analogue (Table 8, entries 13 and 21). Structurally, the dimensions pertaining to **K-VII** and **2** are generally in good agreement (Table 7). The greatest deviance occurs for the K–$N_{TMEDA}$ bonds (mean difference, 0.143 Å), whilst the mean $N_{TMEDA}$-K-$N_{TMEDA}$ angle is 0.65° wider for **2**.

Table 7. Key calculated structural parameters for TMEDA-solvated **M-V**–**M-VIII** and experimentally determined parameters for **2** and **3**.

| | M = Li | M = Na | M = K |
|---|---|---|---|
| **M-V** parameters | | | |
| M–$N_{TMP}$ [Å] | 1.899, 2.086, 1.965 | 2.303, 2.402, 2.249 | |
| M–$N_{TMEDA}$ [Å] | 2.137, 2.230 | 2.516, 2.469 | |
| M···$C_{TMP}$(Me) [Å] | 2.899, 2.938, 3.169, 3.181, 2.865, 2.852 | | |
| M···$C_{TMEDA}$(Me) [Å] | 2.966, 3.041, 3.053, 3.158 | | |
| N-M-N [°] | 170.4, 85.9 | 143.8, 75.9 | |
| M-N-M [°] | 97.7 | 92.3 | |
| **M-VI** parameters | | | |
| M–$N_{TMP}$ [Å] | 1.855 | 2.196 | 2.537 |
| M–$N_{TMEDA}$ [Å] | 2.173, 2.195 | 2.503, 2.507 | 2.870, 3.021 |
| N-M-N [°] | 84.8 | 75.1 | 62.9 |
| **M-VII** parameters | | | |
| M–$N_{TMP}$ [Å] | | 2.441, 2.517 | 2.884, 2.800 |
| M–$N_{TMEDA}$ [Å] | | 2.797, 3.259 | 3.093, 3.095 |
| $N_{TMP}$-M-$N_{TMP}$ [°] | | 104.0 | 78.9 |
| $N_{TMEDA}$-M-$N_{TMEDA}$ [°] | | 62.7 | 61.3 |
| M-$N_{TMP}$-M [°] | | 76.0 | 100.9 |
| **M-VIII** parameters | | | |
| M–$N_{TMP}$ [Å] | | 2.289 | 2.625 |
| M–$N_{TMEDA}$ [Å] | | 2.667, 2.604, 2.774, 5.210 | 2.974, 3.151, 3.018, 3.136 |
| $N_{TMP}$-M-N [°] | | | 60.6, 61.1 |
| X-ray data | compound **3** | | compound **2** |
| M–$N_{TMP}$ [Å] | 1.885(5), 2.049(5), 1.949(5) | | 2.744(2), 2.764(2), 2.836(2), 2.825(2) |
| M–$N_{TMEDA}$ [Å] | 2.121(6), 2.091(6) | | 2.882(2), 3.039(2), 2.934(2), 2.948(2) |
| $N_{TMP}$-M-$N_{TMP}$ [°] | 172.6(3) | | 101.41(4), 101.20(4) |
| $N_{TMEDA}$-M-$N_{TMEDA}$ [°] | 87.0(2) | | 61.83(5), 62.09(4) |
| M-$N_{TMP}$-M [°] | 98.8(2) | | 78.95(4), 78.43(4) |

Table 8. Relative energies of other key calculations.

| | | $\Delta E$ [kcal mol$^{-1}$] |
|---|---|---|
| 1 | **Li-I** + TMEDA → **Li-VI** | −27.06 |
| 2 | **Li-VI** → 1/2 **Li-VII** | +3.87 |
| 3 | 1/2 **Li-II** + TMEDA → 1/2 **Li-VII** | −2.66 |
| 4 | **Li-I** + TMEDA → 1/2 **Li-VII** | −23.18 |
| 5 | 1/4 **Li-IV** + TMEDA → **Li-VI** | −2.47 |
| 6 | 1/4 **Li-IV** + TMEDA → 1/2 **Li-VII** | +1.46 |
| 7 | **Na-I** + TMEDA → **Na-VI** | −22.60 |
| 8 | **Na-VI** → 1/2 **Na-VII** | −4.91 |
| 9 | 1/2 **Na-II** + TMEDA → 1/2 **Na-VII** | −8.19 |
| 10 | **Na-I** + TMEDA → 1/2 **Na-VII** | −27.48 |
| 11 | 1/3 **Na-III** + TMEDA → **Na-VI** | +1.97 |
| 12 | 1/3 **Na-III** + TMEDA → 1/2 **Na-VII** | −2.94 |
| 13 | 1/3 **Na-III** + 2 TMEDA → **Na-VIII** | −0.27 |
| 14 | **Na-VIII** → 1/2 **Na-VII** + TMEDA | −2.67 |
| 15 | **K-I** + TMEDA → **K-VI** | −13.97 |
| 16 | **K-VI** → 1/2 **K-VII** | −11.28 |
| 17 | 1/2 **K-II** + TMEDA → 1/2 **K-VII** | −10.09 |
| 18 | **K-I** + TMEDA → 1/2 **K-VII** | −25.25 |
| 19 | 1/3 **K-III** + TMEDA → **K-VI** | +2.66 |
| 20 | 1/3 **K-III** + TMEDA → 1/2 **K-VII** | −8.62 |
| 21 | 1/3 **K-III** + 2 TMEDA → **K-VIII** | −6.19 |
| 22 | **K-VIII** → 1/2 **K-VII** + TMEDA | −2.43 |
| 23 | **K-I** + 2 TMEDA → **K-VIII** | −22.82 |

## Conclusion

Two new TMEDA-solvated complexes of the synthetically important 2,2,6,6-tetramethylpiperidide anion have been successfully prepared and characterized by X-ray crystallography and NMR spectroscopic studies. These represent the first heavy alkali metal TMP donor-solvates to be studied. In addition, a series of DFT calculations have been performed which enabled us to reason why these complexes are structurally different in comparison to their Li counterparts.

## Experimental Section

**General data**: All reactions and manipulations were carried out in an atmosphere of dry, pure argon gas, using standard Schlenk procedures. Solvents were freshly distilled over Na/benzophenone. NMR samples were prepared under a protective argon atmosphere inside a glovebox using $C_6D_6$ solvent, which was predried over molecular sieves and degassed by using pump-freeze-thaw cycles. BuNa[92] and **3** were prepared as described elsewhere. All NMR spectra were measured on a Bruker DPX400 or AMX400 spectrometer. The X-ray structural determinations were carried out on a Nonius Kappa diffractometer with a CCD area detector using graphite-monochromated $Mo_{K\alpha}$ radiation. CCDC-675683 and 675684 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

**Synthesis of [{(tmeda)Na(tmp)}$_2$] (1)**: Butylsodium (0.16 g, 2 mmol) was suspended in freshly distilled hexane (10 mL). TMPH (0.34 mL, 2 mmol) was introduced to the suspension by using a syringe and the mixture was stirred at ambient temperature for 2 h. The resultant milky-white suspension was treated with three molar equivalents of TMEDA (0.90 mL, 6 mmol) to yield a homogenous yellow solution. The solution was transferred to a freezer operating at −27 °C to yield a crop of colorless needle-like crystals. The crystals redissolved rapidly on removal from the freezer; hence, isolated crystalline yields were modest (0.12 g, 21 %). However, samples were taken of the filtrate and all solvent removed in vacuo with gentle heating to yield a yellow oil at room temperature. NMR spectra of the oil and the crystalline solid were found to correspond to the same material suggesting that the yield is quantitative. $^1$H NMR data ($C_6D_6$, 400.13 MHz, 300 K): $\delta$ = 2.13 (m, 2H; γ-$CH_2$ (TMP)), 1.92 (s, 12H; $CH_3$ (TMEDA)), 1.90 (s, 4H; $CH_2$ (TMEDA)), 1.63 (m, 4H; β-$CH_2$ (TMP)), 1.43 ppm (s, 12H; $CH_3$ (TMP)); $^{13}$C NMR data ($C_6D_6$, 100.62 MHz, 300 K): $\delta$ = 57.6 ($CH_2$ (TMEDA)), 52.8 (α-*C* (TMP)), 46.2 ($CH_3$, (TMEDA)), 42.6 (β-*C* (TMP)), 37.7 ($CH_3$ (TMP)), 21.5 ppm (γ-$CH_2$ (TMP)).

**Synthesis of [{(tmeda)K(tmp)}$_2$] (2)**: A flame-dried Schlenk tube was charged with lithium tetramethylpiperidide (10 mmol, 1.47 g) [prepared

by lithiation of TMP(H)] and potassium *tert*-butoxide (10 mmol, 1.12 g). Hexane (40 mL) was added to these reagents and the mixture was allowed to stir for 12 h. A brown precipitate of KTMP (the lithium *tert*-butoxide by-product was soluble in hexane) was produced, which was collected by Schlenk filtration and subsequently isolated in a glove box (1.47 g, 82%). Subsequently, freshly prepared KTMP (0.36 g, 2 mmol) was suspended in dry hexane (10 mL) and four molar equivalents of TMEDA (1.2 mL, 8 mmol) were introduced to produce a red solution. The solution was filtered and then transferred to a freezer operating at −27 °C. After 48 h, a crop of red, needlelike crystals was deposited from the solution. The crystals redissolved rapidly on removal from the freezer. A suitable crystal was extracted from the solution and immediately coated in Fomblyn inert oil, taken into a stream of cold dry nitrogen at 123 K and the X-ray diffraction data collected. $^1$H NMR data ($C_6D_6$, 400.13 MHz, 300 K): $\delta = 2.05$ (m, 2H; γ-$CH_2$ (TMP)), 2.01 (s, 4H; $CH_2$ (TMEDA)), 1.94 (s, 12H; $CH_3$ (TMEDA)), 1.54 (m, 4H; β-$CH_2$ (TMP)), 1.32 ppm (s, 12H; $CH_3$ (TMP)); $^{13}$C NMR data ($C_6D_6$, 100.62 MHz, 300 K): $\delta = 57.6$ ($CH_2$ (TMEDA)), 52.7 (α-*C* (TMP)), 45.7 ($CH_3$ (TMEDA)), 42.7 (β-$CH_2$ (TMP)), 37.0 ($CH_3$ (TMP)), 21.3 ppm (γ-$CH_2$ (TMP)).

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