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Monomerizing Alkali-Metal 3,5-Dimethylbenzyl Salts with Tris(N, N-dimethyl-2-aminoethyl)amine (Me₆TREN): Structural and Bonding Implications

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Supporting Information

ABSTRACT: The series of alkali-metal (Li, Na, K) complexes of the substituted benzyl anion 3,5-dimethylbenzyl (Me₂C₆H₃CH₂⁻) derived from 1,3,5-trimethylbenzene (mesitylene) have been coerced into monomeric forms by supporting them with the tripodal tetradentate Lewis donor tris(N,N-dimethyl-2-aminoethyl)amine, [N(CH₂CH₂NMe₂)₃, Me₆TREN]. Molecular structure analysis by X-ray crystallography establishes that the cation–anion interaction varies as a function of the alkali-metal, with the carbanion binding to lithium mainly in a σ fashion, to potassium mainly in a π fashion, with the interaction toward sodium being intermediate between these two extremes. This distinction is due to the heavier alkali-metal forcing and using the delocalization of negative charge into the aromatic ring to gain a higher coordination number in accordance with its size. Me₆TREN binds the metal in a η⁴ mode at all times. This coordination isomerism is shown by multinuclear NMR spectroscopy to also extend to the structures in solution and is further supported by density functional theory (DFT) calculations on model systems. A Me₆TREN stabilized benzyl potassium complex has been used to prepare a mixed-metal ate complex by a cocomplexation reaction with tBu₂Zn, with the benzyl ligand acting as an unusual ditopic σ/π bridging ligand between the two metals, and with the small zinc atom relocalizing the negative charge back on to the lateral CH₂ arm to give a complex best described as a contacted ion pair potassium zincate.

INTRODUCTION

Diversity of aggregation is a defining feature of organo alkali-metal chemistry and is dependent on the identity of both the alkali-metal and the organo-anion. The understanding of aggregation state allows one to rationalize rates of reactivity since there is a strong correlation between the two. The most obvious example is that tBuLi is more reactive than nBuLi in hydrocarbon solvents because the former is predominantly a tetramer; while the latter is predominantly a hexamer in this Lewis donor free medium. Solvation of transition states may also play a critical role in this reaction rate modification. Therefore, given the pervasive nature of organo alkali-metal reagents throughout synthetic chemistry, it is highly important to understand aggregation as a prelude to understanding reactivity. This rich diversity is of course increased when a third factor is introduced, namely, the presence of a Lewis basic neutral coligand. These tend to be simple molecules such as commercially available ethers (e.g., diethyl ether, Et₂O; tetrahydrofuran, THF; dimethoxyethane, DME) or amines (e.g., N,N,N′,N′-tetramethylthlyenediamine, TMEDA) which have the effect of deaggregating the organo alkali-metal reagent, with the typical knock-on effect being an increase in reactivity.

Recently, we have been drawn to the use of coordinately flexible tris(N,N-dimethyl-2-aminoethyl)amine (Me₆TREN, Figure 1) as a useful bonding probe in organo alkali-metal chemistry since this tripodal tetra-amine can effectively shield an entire hemisphere of the alkali-metal, leaving only a small coordination arc through which it can interact with a charge neutralizing organoanion.

Figure 1. ChemDraw representation of Me₆TREN.
This generally encourages the formation of highly reactive monomeric species, since the blocking of the potential bonding sites of the alkali-metal from the organoanion prevents the formation of the three-center-two-electron (electron deficient) bonds which propagate oligomerization. This simple way of designing a monomer thus inhibits all secondary bonding and gives an unequivocal view of the primary cation—anion bonding interaction which is taking place. We recently displayed this principle in practice with the monomeric series PhCH₂M·Me₃TREN (M = Li, Na, K, TREN) which showed that the localizing effect of the alkali-metal on the negative charge is gradually diminished as the alkali-metal size is increased; that is the M-anion bonding changes from mainly σ (sp³ CH₂) to mainly π (sp² CH₂) on going from small Li to large K. By studying the bonding picture in the potassium example 3 it could be surmised that the secondary interaction in the polymeric structure of the related complex [PhCH₂K·PMDETA]∞ (Figure 2) is in fact the σ-bond between the CH₂ arm and K rather than the π-bond between the aromatic ring and the metal.

![ChemDraw representation of molecular structures of [PhCH₂K·PMDETA]∞ (left) and PhCH₂K·Me₃TREN (3) monomer (right).](image1)

Reported in a communication, this series of benzyl complexes also represented somewhat of a landmark in alkali-metal chemistry in that the three complexes all contained the same anion, donor, and aggregation state, which up until that point had proved impossible because of the significant differences in ionic radii of the alkali-metals (which tends to result in either different aggregation states and/or different numbers of solvating ligands being involved). Following on from this initial discovery, in this full paper we have taken these studies further to investigate if the above bonding situation was a unique case or whether it could be extended into more challenging substituted benzyl alkali-metal systems. Furthermore, we have probed our findings via density functional theory (DFT) calculations which show excellent agreement with the experimental outcomes.

### RESULTS AND DISCUSSION

#### Synthesis of Me₃Bn Alkali-Metal Me₅TREN Monomers.

Synthetically we commenced by preparing complexes of general formula Me₃BnM·Me₅TREN (M = Li, Na, K, TREN; Me₃Bn = 3,5-dimethylbenzyl, C₇H₁₅; see eq 1 for details) in an effort to ascertain whether the benzyl complexes mentioned earlier were a special case or if the bonding seen previously in complexes 1–3 can be considered as representative of benzyl alkali-metal monomers in general. For the lithium complex, a direct deprotonation method was employed whereby nBuLi was simply added to a solution of Me₅TREN in bulk mesitylene (1,3,5-trimethylbenzene) with the colorless solution immediately turning orange. For its heavier congeners, a Lochmann–Schlosser approach was taken with the insoluble Me₃BnM solid prepared by introducing nBuLi to a hexane solution containing mesitylene and the appropriate heavier alkali-metal tert-butoxide MOtBu (M = Na, K). The resulting orange or red colored powder was filtered, washed with hexane to remove soluble LiOtBu, and dried under reduced pressure. The powder was subsequently suspended in mesitylene and two molar equivalents of Me₅TREN were then added via syringe to give an intensely colored solution.

All solutions yielded X-ray quality crystalline material upon cooling to −30 °C. The molecular structures were thus determined (see Figures 3–5: with pertinent bond parameters shown).

![Molecular structure of Me₃BnLi·Me₅TREN (4).](image2)

![Molecular structure of Me₃BnNa·Me₅TREN (5).](image3)

![Molecular structure of Me₃BnK·Me₅TREN (6).](image4)
The transition from a localized negative charge in a benzylic type anion to a delocalized negative charge is typically accompanied by a deformation of the aromatic ring. In particular the \( C_{ipso} - C_{ortho} \) and \( C_{meta} - C_{ipso} \) bonds are elongated and the \( C_{ortho} - C_{meta} \) bonds are shortened from the ideal aromatic length of 1.4 Å for aromatic C–C bonds, as explained previously by Feil and Harder. While the extent of this deformation noticeably increased moving through the series 1–3, it is not particularly evident in 4–6 (Figure 6). This must be a consequence of the additional electron releasing Me substituents at the \( \eta_6 \) positions, which reduce deformation of the aromatic ring caused by the resonance delocalization. However, this smaller electronic perturbation within the carbon framework does not impede the potassium, and to a lesser extent the sodium from taking up steric positions that maximize their coordination numbers in line with their sizes.

The similarity of the aromatic ring bond parameters in complexes 4–6 is unsurprisingly repeated in their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMOs) (Figure 11, see calculation section for full details).

Interestingly, complex 4 is considerably removed from the only previous 3,5-dimethylbenzyl alkali-metal complex to be characterized crystallographically. With the only distinction being the identity of the polydentate amine donor (in this case bidentate TMEDA - \( \text{N}_2\text{N}_2\text{N}_2\text{N}_2\text{-tetramethylethlenediamine} \)), the previously reported complex \( ([\text{TMEDA}]\text{Li})^+[([\text{Me}_2\text{Bn}]\text{Li-TMEDA}^-) \) adopts a solvent separated lithium salt structure, in which a lithium atom resides in both cationic and anionic moieties (Figure 7).

The two dimethylbenzyl ligands in this litiath display noticeably different bonding to the lithium center. The first can almost be considered as being \( \eta^2 \) bound, with the \( \text{Li}^-\text{C}_n \) and \( \text{Li}^+\text{C}_{ipso} \) distances of 2.257(2) and 2.637(6) Å (giving a ratio of 1.17, similar to that seen in our Na complex 5, 1.14) and a \( \text{Li}^+\text{C}_n - \text{C}_{ipso} \) angle of 89.0(3)°. Meanwhile, the second ligand displays parameters more in line with those of lithium complex 4, specifically \( \text{Li}^+\text{C}_n \) and \( \text{Li}^+\text{C}_{ipso} \) bond lengths of 2.325(7) and 3.757(2) Å (ratio 1.45) and a \( \text{Li}^+\text{C}_n - \text{C}_{ipso} \) angle of 127.8(3)° (cf. 4, \( \text{Li}^+\text{C}_n \) 2.388(2); \( \text{Li}^+\text{C}_{ipso} \) 3.453(2) Å; ratio 1.45; \( \text{Li}^+\text{C}_n - \text{C}_{ipso} \) 128.85(10)°) and can thus be unequivocally assigned as being \( \eta^2 \) bound.

Power has reported the THF solvated mesityl (isomeric with our anion) lithium cyclo-dimeric complex \( (\text{LiMes-2THF})_2 \), however in this the metal is bound to a ring carbon rather than

### Table 1. Selected Bond Parameters for Experimental \( \text{Me}_2\text{TREN} \) Complexes 3–6 and \( \text{ZnBu}_3 \) and Their DFT Models

<table>
<thead>
<tr>
<th>Complex</th>
<th>( r_{4} )</th>
<th>( s_{6} )</th>
<th>( s_{6} )</th>
<th>( s_{6} )</th>
<th>( s_{6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M}_1\text{–C}_20 )</td>
<td>2.388(2)</td>
<td>2.115</td>
<td>2.568(2)</td>
<td>2.526</td>
<td>3.627(3)</td>
</tr>
<tr>
<td>( \text{M}_1\text{–C}_21 )</td>
<td>3.453(2)</td>
<td>3.156</td>
<td>2.936(2)</td>
<td>3.008</td>
<td>2.954(2)</td>
</tr>
<tr>
<td>( \text{M}_1\text{–C}_21/\text{M}_1\text{–C}_20 )</td>
<td>1.45</td>
<td>1.42</td>
<td>1.14</td>
<td>1.19</td>
<td>0.81</td>
</tr>
<tr>
<td>( \text{C}_20\text{–C}_21 )</td>
<td>1.412(2)</td>
<td>1.446</td>
<td>1.405(2)</td>
<td>1.429</td>
<td>1.388(4)</td>
</tr>
<tr>
<td>( \text{M}_1\text{–N}_1 )</td>
<td>2.302(2)</td>
<td>2.457</td>
<td>2.542(1)</td>
<td>2.647</td>
<td>2.953(2)</td>
</tr>
<tr>
<td>( \text{M}_1\text{–N}_2 )</td>
<td>2.191(2)</td>
<td>2.334</td>
<td>2.524(1)</td>
<td>2.564</td>
<td>2.786(2)</td>
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<tr>
<td>( \text{M}_1\text{–N}_3 )</td>
<td>2.181(2)</td>
<td>2.301</td>
<td>2.524(2)</td>
<td>2.590</td>
<td>2.781(3)</td>
</tr>
<tr>
<td>( \text{M}_1\text{–N}_4 )</td>
<td>2.288(2)</td>
<td>2.457</td>
<td>2.480(1)</td>
<td>2.613</td>
<td>2.802(2)</td>
</tr>
<tr>
<td>( \text{M}_1\text{–C}_20\text{–C}_21 )</td>
<td>128.85(10)</td>
<td>116.3</td>
<td>90.41(10)</td>
<td>95.0</td>
<td>50.88(14)</td>
</tr>
<tr>
<td>( \text{K} \text{–Ar} )</td>
<td>2.798(1)</td>
<td>2.886(1)</td>
<td>2.830(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Zn}_1\text{–C}_20 )</td>
<td>2.109(4)</td>
<td>2.220</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Zn}_1\text{–C}_13 )</td>
<td>2.044(3)</td>
<td>2.042</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{Zn}_1\text{–C}_27 )</td>
<td>2.045(3)</td>
<td>2.048</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
propagating through $\eta^6$ structure of unsolvated MesLi as a completeness that Lerner et al. have reported the molecular complexes as described herein (see Figure 8). We note for substituted phenyl complexes rather than substituted benzyl a lateral one, giving such a structure more in common with Figure 7. ChemDraw representation of molecular structure of Figure 6. Resonance forms for the anion in complexes 4–6 (top) and their C–C bond lengths (in Å) (below).

lithium centers and the $\pi$ system of an adjacent mesityl ring as shown above. Also, Davies has reported an excellent series of papers applying the mesityl lithium moiety within a bimetallic Li/Cu framework, although again the metal–carbon contact is through a ring carbon (to copper) with Li binding to the $\pi$ face of the mesityl anion. Specifically in Cu$_2$Li$_3$(Mes)$_2$(NBn)$_2$, $\eta^6$ binding, similar to our K based complexes 3 and 6 is seen. Meanwhile, in Cu$_2$Li(Mes)$_2$ the binding is $\eta^6$/ipso to an aryl ring above and below the metal with the metal lying above the center of the ring while in Cu$_2$Li$_3$(Mes)$_4$ a more “slipped” arrangement occurs with a $\eta^6$/ipso bonding mode in place (that is with the ipso carbon of the second ring lying directly below the lithium atom).

On perusing bond parameters of other crystallographically characterized alkali-metal benzyl complexes it is discernible that there is a considerable amount of $\eta^5$ bonding character in the lithium and sodium complexes described thus far, that is, where the benzyl anion has at least a minor degree of interaction between the ipso carbon and the metal, which is expressed most clearly by the C$_{ipso}$–C$_{ipso}$–M bond angle. Lithium benzyl complexes can be placed in three aggregation categories; namely, monomeric, cyclotetrameric, and polymeric, with sodium congeners also providing cyclotetrameric and polymeric examples. However, regardless of the aggregation state, this C$_{ipso}$–C$_{ipso}$–M bond angle tends to deviate no more than 15° from a right angle. While this also holds true for our sodium monomers 2 and 5, lithium monomers 1 [mean such angle 129.9°] and 4 [128.85 (10)°] have a more typical sp$^3$ type of bonding. We assume this can be ascribed to their greater coordination number (5) as the previously reported monomers each have a coordination number of 4, namely, with THF/TMEDA, Me$_6$TACN (N$^N$N$^N$N$^N$-trimethyl-1,4,7-triazacyclononane) or PMDETA acting as the neutral Lewis donor. However, it is worth noting that the Me$_6$TREN molecule is disposed in such a way that a NMe$_3$ group does not lie directly above the C$_{ipso}$–C$_{ipso}$ bond, minimizing steric inhibition of a C$_{ipso}$–Li interaction [smallest C–C–Li–N torsion angles are S5.370 (18) and S5.36 (15)° for 1 and 4 respectively]. In our sodium monomers 2 and 5, the C$_{ipso}$–C$_{ipso}$–M angle has reduced to 103.3 (1) and 90.41 (10)° respectively, much more indicative of $\eta^5$ coordination to the metal. This is despite a NMe$_3$ group now lying directly above the C–C bond which one would expect would hinder such coordination [smallest C–C–Na–N torsion angles are now 12.56 (10) and 16.68 (12)° for 2 and 5 respectively]. The longer C–M bond distance presumably thus
plays a role in allowing such a bonding arrangement to take place. A comparison of the Me₆TREN alignments with respect to the mesityl anion of 4 and 5 is shown in Figure 9. There is no obvious reason for the disparity in C_{ipso}−C_{α}−Na angles for 2 and 5, with the methyl groups an unlikely candidate because of their relatively small bulk and remoteness from the carbanionic center, and it is thus perhaps more likely to be due to a crystal packing effect.

The structural pattern witnessed in the solid state appears to be replicated in solution as evidenced by perusal of ¹H NMR data, collected in C₆D₆ solution (summarized in Table 2). The delocalization of the negative charge from the CH₂ arm into the aromatic ring is manifested in the NMR spectrum in two principal ways; the first is the greater shielding of the aromatic proton resonances by the electropositive metal as group 1 is descended and is quite clearly occurring here as demonstrated by the ortho and para chemical shifts listed in Table 2. The second way is through the C−H coupling of the “metalated” CH₂ arm, which can be discerned either from observing the ¹J(C−H) satellites in the ¹H NMR spectrum (provided it is in an uncluttered region of the spectrum as they are only 1% intensity) or through collecting a ¹³C (¹H coupled) spectrum. Boche¹⁸a has previously reported that this coupling constant will be approximately 125 Hz for a perfectly pyramidalized sp³ system (one with a σ-bound metal such as in 4) and will rise toward 167 Hz as sp² hybridization is approached (that is as in the π bonding situation present in 6). This sequential increase in the coupling constant is indeed evident, altering from 133 Hz in 4 to 144 Hz in 5 and finally to 150 Hz in 6. These values are similar to those witnessed for complexes 1−3 (131, 142, and 150 Hz, respectively) and suggest that the presence of the extra methyl groups on the aromatic ring have only a negligible effect on the hybridization. The change of hybridization as a function of alkali-metal is further supported by the downfield shift of the CH₂ group resonance away from the alkyl region and toward the olefinic as shown in Table 2. Interestingly, the ¹H NMR spectrum of 6 bears little similarity to that of 3,5-dimethylbenzyl potassium in THF (ortho, 6.69; para, 5.23; methyl, 2.19; CH₂, 1.63 ppm),¹³ suggesting that the bonding is considerably different in these complexes.

Kays and co-workers recently reported a pair of lithium carbazol-9-yl complexes. The THF solvated monomer (with no Li−π interactions) gave a ⁷Li NMR resonance at −1.1 ppm

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**Table 2. Selected ¹H NMR Chemical Shift Data (ppm, 400.13 MHz) for Complexes 4−6 in C₆D₆ Solution**

<table>
<thead>
<tr>
<th></th>
<th>mesitylene</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>3−ZnBu₂</th>
<th>3⁻</th>
</tr>
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<tbody>
<tr>
<td>ortho</td>
<td>6.72</td>
<td>6.38</td>
<td>6.21</td>
<td>5.90</td>
<td>7.05</td>
<td>6.16</td>
</tr>
<tr>
<td>meta</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.85</td>
<td>6.56</td>
</tr>
<tr>
<td>para</td>
<td>6.72</td>
<td>5.83</td>
<td>5.54</td>
<td>4.95</td>
<td>6.29</td>
<td>5.24</td>
</tr>
<tr>
<td>CH₃⁻</td>
<td>2.16</td>
<td>2.32</td>
<td>2.49</td>
<td>3.27</td>
<td>2.32</td>
<td>3.21</td>
</tr>
<tr>
<td>¹J(CH) (Hz)</td>
<td>133</td>
<td>144</td>
<td>150</td>
<td>127</td>
<td>151</td>
<td></td>
</tr>
</tbody>
</table>

¹CH₃

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**Figure 9.** Alternative view of molecular structures of 4 (left) and 5 (right).

**Figure 10.** Optimized structures of complexes 4 (M = Li; left), 5 (M = Na; middle), and 6 (M = K; right).
while the unsolvated dimer (which dimerizes through a Li–π interaction) gave the corresponding resonance much further upfield at −5.9 ppm because of shielding of the lithium cation by the aromatic π-system. Thus the 1H NMR resonance of 4 at 0.83 ppm is perhaps indicative that there is no Li–π interaction in solution.

Overall, from the combination of solid state and solution evidence witnessed in these two series we contend that such a pattern of bonding between the alkali-metals and CH$_2$–Ar anions is probably a general phenomenon in the absence of other structure influencing functional groups.

**DFT Calculations.** To probe further the coordination isomerism at play in the alkali-metal mesityl complexes 4–6 (and indeed the benzyl complexes 1–3) we turned to DFT calculations. The optimized energy minimum structures supported our experimental observations of coordination isomerism with the alkali-metal clearly migrating from being σ bound to the CH$_2$ group to being π bound to the aromatic ring as the group was descended. These configurations resulted even when the alkali-metal was deliberately forced in the calculation to start in the “wrong” coordination site, that is, with Li binding to the π system of the aryl ring and potassium σ bound to the CH$_2$ group. The optimized structures of 4–6 are displayed in Figure 10 with selected calculated bond parameters in Table 1. Those of 1–3 are available in the Supporting Information.

While the bonding trends already witnessed in the experimental structures are essentially replicated in the DFT calculations, the calculations predict a stronger cation–anion interaction and a concomitantly weaker cation-Lewis donor interaction. This is primarily evidenced by the calculated M–CH$_2$ distances which are all shorter than determined experimentally (by 0.173, 0.042, and 0.222 Å for 4, 5, and 6, respectively), while the M–N$_{donor}$ distances are all predicted to be longer than in complexes 4–6 (Table 1). The general trends of the calculated parameters however all mirror those of the experimental molecular structures. Specifically, our calculations suggest that the unique M–N bond (that is the one to the unique central nitrogen atom of Me$_2$TREN) will be the longest of these in each case, while they also intimated that complex 4 will display a considerable disparity in M–N$_{Me}$ distances (two shorter and one longer) but that the M–N$_{Me}$ bonds will all be similar in complex 5 and also in complex 6. Further, the structures of 4$_{alk}$ and 5$_{alk}$ confirm the different rotation of the tripodal ligand with respect to the CH$_2$–C$_{gypo}$ bond, with a staggered arrangement occurring in the lithium example (C–C–Li–N = 40.4°) and approaching a more eclipsed arrangement in the sodium congener (C–C–Na–N = 22.7°).

Next, we considered the atomic charges and bond indices for the series of complexes 1–6. The charge distribution was obtained via a Natural Bond Orbital (NBO) analysis. The results of this (as displayed in Table 3) overwhelmingly corroborated the trends witnessed in the experimentally observed molecular structures. Specifically, we can see that there is a small but significant change in the distribution of charge as the metal is changed from Li to Na and then to K. Unsurprisingly as the group is descended, the positive charge on the metal increases in line with increasing electropositivity from +0.84 (Li) to +0.87 (Na) and to +0.90 (K). However, the negative charge distribution alteration is more pronounced. On moving from Li to Na (which results in only a small movement of the metal as seen by the change in the C–C–M angle, vide supra) the charge on the CH$_2$ group alters modestly from −0.94 to −0.87. However, on moving to the potassium congener which is considerably removed from the CH$_2$ arm, the negative charge located here reduces to −0.67. Concomitantly we see an increase in the sum of negative charge on the aromatic carbon atoms as the metal migrates, confirming that the charge is being more delocalized to the ring. We note in relation to this that Stalke and co-workers showed the localizing effect of a basic heteroatom in their related 2-picolyllithium complexes, which have the negative charge predominantly localized on the *ortho*-nitrogen atom (−1.04) and only −0.19 on the methylene carbon atom.

Perusing the bond indices suggests that there is very little covalent bonding character in the M–C bonds, suggesting that the bonding between cation and anion is more ionic (electrostatic) in nature. This effect is most pronounced in the M–CH$_2$ bond indices which are extremely small (range 0.02–0.06). What is also clear is that the bond index value for the CH$_2$–C$_o$ bond increases as the metal size increases, in agreement with the fact that this bond decreases in length as the series is crossed. Likewise, the C–C$_i$ and C–C$_ip$ bond indices decrease while those of the C–C$_ip$ bonds increase, emphasizing the ring deformation which occurs upon charge delocalization as described previously by Harder (vide supra).

We also studied the molecular orbitals of complexes 1–6. Those frontier orbitals of the substituted benzyl derivatives 4–6 are displayed in Figure 11 while those of the benzyl complexes 1–3 are provided in the Supporting Information. As mentioned earlier, they are essentially the same regardless of the identity of the alkali-metal (and by extension regardless of the mode of cation–anion interaction).

Specifically, the HOMO of each is the highest filled π system of the benzyl anion while the LUMO is located on the Me$_2$TREN donor which encapsulates the alkali-metal. This similarity would suggest that even though the location of the alkali-metal cation and the location of the negative charge in the anion (localized at the CH$_2$ or delocalized through the aromatic ring) differs, the seat of reactivity in, for example, an electrophilic quench would result in the electrophile binding...
at the same position for each example, specifically in these cases at the CH₂ group.

**Synthesis of Heterobimetallic Complex.** With this part of the study complete and given our ongoing interest in bimetallic frameworks containing alkali-metals, we contemplated what effect the use of a π-bound organo alkali-metal reagent would have. For ease of synthesis we reverted to using unsubstituted benzyl complex 3 (PhCH₂K·Me₃TREN) and opted for zinc (specifically tBu₂Zn) as the second metal. Complex 3 was prepared in situ in toluene,7 and a toluene solution containing one equivalent of tBu₂Zn was added via cannula with stirring. The deep red color of the solution was seen to pale but not completely dissipate. After reducing the volume the solution was cooled to deposit X-ray quality crystals of a new complex, tBu₂Zn(PhCH₂)·Me₃TREN (3-ZnBu₂), the molecular structure of which is shown in Figure 12.

This revealed that while the resulting complex is bimetallic, it does not adopt the type of motif typically seen in alkali-metal metallates. Rather than bridging between the two metals through a single point, as is the case in the related bis-TMEDA metallates. Rather than bridging between the two metals does not allow the two metals to be linked via two anionic bridges as is typically the case, although this may also in part be attributed to the monomerizing ability of Me₃TREN ligand blocking any potential ligating sites on potassium. We identified two possible ways of describing 3-ZnBu₂, either as a cocomplexation of two neutral moieties (that is of type [PhCH₂K·Me₃TREN]·[ZnBu₂] with the negative charge still delocalized in the aromatic ring) or a pseudoassociated ion pair (that is of type [K·Me₃TREN]⁻·[PhCH₂ZnBu₂]⁺ with the negative charge relocalized on the CH₂ arm and the “solvent separated” K cation having its coordination shell completed by the aromatic system of the benzyl group in the absence of other Lewis donating solvents). To ascertain which of these descriptions was the more apt we turned to both the solid state bond parameters and solution NMR data, comparing values for this new complex with homometallic 3 (Tables 1 and 2, bond parameters in Table 1 represent the major component of one of the independent molecules within the unit cell). These suggested that it is the latter, “ate” situation, which is arising here. Primarily this is attributed to the increase in the K–C_centroid distance upon addition of ZnBu₂ [c.f. 2.868(1) Å versus 2.830(1) Å in 3], which has a concomitant effect of shortening the K–N distances (mean 2.819 Å versus 2.848 Å in 3) since the now formally neutral aromatic ring exerts less of a pull on the cation. This distance is slightly shorter than that of another K’-benzyl interaction 2.940(1) Å in Jones’ Ga(II) complex where the potassium counterocation is solvated by a gallium bound benzyl group and three molecules of diethyl ether.29 We note at this juncture that the K–C_centroid distances of the crystallographically characterized supramolecular [K-(arene)₃]⁺·[M(HMDS)_3]⁻ (M = Mg, arene = toluene, o-xylene; M = Zn, arene = p-xylene) are in the range 2.884—3.023 Å.30 Furthermore, there is a clear lengthening of the diagnostic C20—C21 bond [c.f. 1.469(8) Å versus 1.390(6) Å in 3] consistent with relocalization of the negative charge at C21 reducing the olefinic nature of this bond. The trigonal planar environment around the zinc atom mirrors that in the related complex tBu₂Zn(PhCH₂)Na₂TMEDA.28 Our complex also bears close resemblance to the amide rich potassium zincate [KZn(HMDS)₃(CH,Ph)]⁺⁻ formed by the synergic deprotonation of toluene by the homoleptic base KZn(HMDS)₃ (HMDS = 1,1,1,3,3,3-hexamethyldisilazide, N(SiMe₃)₃).31 In this complex the zinc center is also in a distorted trigonal planar environment surrounded by the benzyl CH₂ group and two nitrogen atoms of HMDS. Potassium is π bound to the arene ring with the K–C_centroid distance of 2.919 Å being marginally longer than in 3-ZnBu₂. In the absence of neutral Lewis donors the potassium atom binds to the HMDS nitrogen atoms, with these bridging amides propagating a polymeric structure.

In solution the relocalization of the negative charge at the CH₂ arm is manifested through a considerable downfield shift of the aromatic proton resonances (from 6.16, 6.56, and 5.24 ppm in 3 to 7.05, 6.85, and 6.29 ppm in 3-ZnBu₂ for the ortho, meta, and para resonances, respectively) and a concomitant upfield shift of the resonance of the CH₂ arm itself from 3.21 ppm in 3 to 2.32 ppm in 3-ZnBu₂. The 1JCH coupling constant is also significantly decreased from 151 Hz in the absence of tBu₂Zn to 127 Hz in its presence, clearly now more at the sp³ hybridization end of the spectrum.

**DFT Calculations.** DFT calculations also supported the assignment of this complex as a potassium zincate structure. As shown in Figure 13 the calculations agree with the experimental
finding that the minimum energy structure is a contacted bimetalllic structure with the benzyl anion bridging between the tBu2Zn and K-Me6TREN moieties in a σ/π fashion. As before, the calculations slightly overestimate the strength of the K−Ph interaction as evidenced by the C−K bond lengths (3.684 and 3.010 Å for K−CH2 and K−Cipso respectively), with a concomitant underestimation of the K−N donor distances (mean 2.935 Å; mean observed in 3-ZnBu2 2.819 Å). The calculated structure predicts a lengthening of the CH2−Cipso bond distance (1.438 Å) with respect to the parent homometallic potassium complex (3) although this is predicted to be marginally shorter than the experimentally determined value of 1.469(5) Å. The effect of this is to again overestimate the CH2−Zn distance by almost 0.1 Å.

**EXPERIMENTAL SECTION**

**General Experimental Procedures.** All reactions and manipulations were carried out under a protective argon atmosphere using either standard high vacuum Schlenk techniques or an MBraun glovebox fitted with an inert gas recirculation and purification system. Hexane was dried over Na/benzophenone and freshly distilled prior to use. Mesitylene was distilled and stored over 4 Å molecular sieves. MesNa and MesK were made from a superbasic nBuLi/MOBF mixture in mesitylene/hexane and collected by filtration and dried in vacuo. nBuLi (1.6 M in hexanes) and MOBF were purchased from Aldrich and Alfa Aesar respectively and used as received.

NMR spectra were collected on a Bruker AV400 MHz spectrometer operating at 400.13 MHz for 1H, 155.47 MHz for 2Li, and 100.62 MHz for 13C. All 13C NMR spectra were proton decoupled. Adequate elemental analyses of complexes 4−6 could not be obtained because of difficulty in completely removing poorly volatile mesitylene under reduced pressure coupled with acute air and moisture sensitivity. 1H NMR spectra are provided in Supporting Information as alternative proof of bulk purity.

**Table 4. Crystallographic Data and Refinement Details for Complexes 4−6, 3-ZnBu2**

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<th>6a</th>
<th>3-ZnBu2b</th>
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<tr>
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<td>C21H14LiN4</td>
<td>C21H24NaN4</td>
<td>C21H24KN4</td>
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<tr>
<td><strong>mol. mass</strong></td>
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<td>372.57</td>
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<tr>
<td><strong>a/Å</strong></td>
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<td>17.9031(11)</td>
<td>14.6284(10)</td>
<td>14.6284(10)</td>
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<td><strong>b/Å</strong></td>
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<td>8.6147(5)</td>
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<td>8.9408(5)</td>
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<tr>
<td><strong>c/Å</strong></td>
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<td><strong>β/deg</strong></td>
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<td>112.510(7)</td>
<td>96.123(2)</td>
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<td><strong>observed reflns [1 &gt; 2σ(I)]</strong></td>
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<td>4622</td>
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<td>9380</td>
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<tr>
<td><strong>2θmax/deg</strong></td>
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<td><strong>no. of parameters</strong></td>
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<td>244</td>
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<td><strong>R [on F2, obs reflns only]</strong></td>
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<td><strong>wR [on F2, all data]</strong></td>
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<td><strong>largest diff. peak/hole/e Å−3</strong></td>
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<td>0.267/−0.209</td>
<td>0.662/−0.846</td>
<td>0.562/−0.325</td>
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</table>

“Reflection data for 6 was twinned by a 180° rotation about 0 0 0. This was accounted for by reprocessing to give a SHELX hklf 5 formatted reflection file. BASF refined to 0.258. “Both independent TREN ligands and one of the tertiary butyl ligands were modeled as disordered, each over two sites.

**CONCLUSION**

In conclusion, we have now shown that alkali-metal benzyl complexes consistently display a noticeable variation in their metal-anion coordination mode depending on the identity and thus the size of the metal, altering from a strictly σ M−C bond for lithium to more of an aromatic π interaction for potassium. Such changes are clearly evident in both the solid state and also in solution, the latter case being discernible by both the change in chemical shift of the CH2− resonance as well as the magnitude of the CH coupling constant of this functionality. This structural variation is supported by DFT calculations.

Finally, when utilized as part of a bimetalllic (Zn/K) system, the benzyl anion acts as a dual σ/π ligand bridging between the two metals with experimental evidence suggesting that the negative charge has been relocalized onto the CH2− group resulting in a potassium zinicate complex.

Figure 13. Optimized energy minimum structure of complex 3-ZnBu2.
Me$_n$LiMe$_n$TREN (4). nBuLi (1.0 mL, 1.6 M in hexanes, 1.6 mmol) was added via syringe to a stirring solution of Me$_n$TREN (0.41 mL, 1.6 mmol) in mesitylene (5 mL), immediately changing the solution color from colorless to orange. A narrow tube containing pentane was left in the flask which was cooled to 4 °C to yield a crop of X-ray quality orange crystals. Yield 0.271 g, 47%.

Me$_n$NaMe$_n$TREN (5). MesNa (0.142 g, 1 mmol) was suspended in mesitylene (5 mL), and Me$_n$TREN (0.52 mL, 2 mmol) was added via syringe. After sonication for 10 min an intensely colored solution formed using the Gaussian broad s, Me$_n$TREN CH$_3$. This was prepared in the same manner as Me$_n$K (0.158 g, 1 mmol). Yield 0.212 g, 59%.

These were filtered, washed with cold hexane, and dried in vacuo. Yield 0.159 g, 42%.

H NMR (CD$_2$OD, 300 K): δ 6.21 (2H, s, ortho CH), 5.54 (1H, s, para CH), 2.50 (2H, s, Li-CH$_2$), 2.25 (s, 6H, mesityl Me), 2.02 (18H, s, Me$_n$TREN Me + CH$_3$), 1.86 ppm (6H, t, Me$_n$TREN CH$_3$).

Selected crystallographic and re

Theoretical Calculations. DFT calculations were performed using the Gaussian computational package G03. In this series of calculations the B3LYP density functional and the 6-311G(d,p) basis set were used. After each geometry optimization, a frequency analysis was performed.

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