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ARTICLE

Heterobimetallic metallation studies of *N,N*-dimethylphenylethylamine (DMPEA) : benzylic C-H bond cleavage/dimethylamino capture or intact DMPEA complex†‡

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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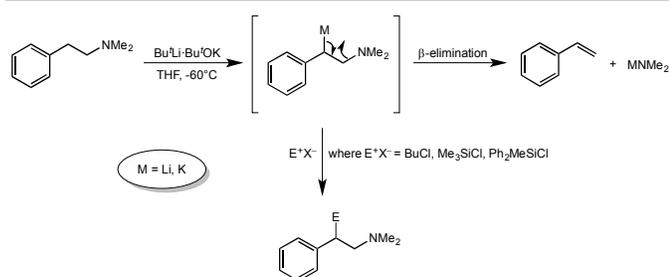
Reaction of the sodium monoamido-bisalkylzincate [(TMEDA)Na(TMP)(Bu^t)Zn(Bu^t)] (TMEDA is *N,N,N',N'*-tetramethylethylenediamine; TMP is 2,2,6,6-tetramethylpiperidide) and the related lithium zincate [(PMDETA)Li(TMP)Zn(Bu^t)₂] (PMDETA is *N,N,N',N'',N''*-pentamethyldiethylenetriamine) with the sensitive bio-relevant scaffold *N,N*-dimethylphenylethylamine, DMPEA, afforded the crystalline complexes [(TMEDA)Na(TMP)(NMe₂)Zn(Bu^t)] and [(PMDETA)Li(NMe₂)Zn(Bu^t)₂], respectively, both of which have been characterized by NMR spectroscopic and X-ray crystallographic studies. Made by reaction of a LiTMP/(TMP)Al(Bu^t)₂ mixture with DMPEA, a third dimethylamino-containing crystalline complex, the aluminate [(THF)Li(TMP)(NMe₂)Al(Bu^t)₂] has been similarly characterized. All three complexes can be regarded as products of cleave and capture chemistry whereby metallation at the benzylic position of DMPEA has led to a β-elimination of an anionic Me₂N fragment that has been captured by a charge balancing cationic heterobimetallic entity. While a metallated intermediate prior to the elimination has proved elusive in all of these reactions, DMPEA has been captured fully intact in the novel Lewis acid – Lewis base crystalline complex [DMPEA·Li(TMP)Zn(Me)₂], which has also been characterized by the aforementioned techniques.

Introduction

As highlighted by the recent publication of a book dedicated to the topic,^[1] synergistic effects of bimetallic compounds (or reagents) are increasingly attracting the curiosity of chemists. What captivates their imagination in particular are examples where the combination of different metals and/or different ligands can cooperatively realize useful chemistry that is seemingly impossible for the individual metal-ligand species. Focusing on metallation (metal-hydrogen exchange) chemistry, approaching its 50th birthday, the Lochmann-Schlosser superbase,^[2-5] formulated as BuⁿLi·Bu^tOK, could be considered an early exemplar of a mixed-metal, mixed-ligand synergistic system as its reactivity generally cannot be matched by its individual alkylolithium or potassium alkoxide components. However, the timeline of such synergistic chemistry stretches back much further to the epochal 1858 discovery of the first alkali metal zincate [Na(ZnEt₃)] by Wanklyn.^[6] This follows since metallate (ate) complexes (e.g., magnesiates, zincates,

aluminates)^[7-8] by their very definition must be synergistic species as they contain two (or more) distinct metals that in contacted ion pair structures would both be involved in the transition states of reaction intermediates or in solvent-separated structures facilitate the charge separation by the alkali metal transferring its valence electron to the more electronegative softer metal (e.g., magnesium, zinc or aluminium). In principle, the neutral magnesium, zinc or aluminium components of these compounds, when separated from the alkali metal moieties, cannot reproduce these features (note, however, that homometallic lithium lithiates and potassium potassiates are known^[9-13]) and so are extremely weak bases generally incapable of deprotonating aromatic molecules. A recent example of a synergistic reaction that caught our eye was Strohmann's report^[14] of the "sedated metallation" (that is to metallate the desired bond but also to stabilize the resulting carbanion) of the sensitive tertiary amine *N,N*-dimethylphenylethylamine, DMPEA (also called 2-phenylethyldimethylamine) by the modified Lochmann-

Schlosser superbases $\text{Bu}^t\text{Li} \cdot \text{Bu}^t\text{OK}$ (Scheme 1). DMPEA is of particular interest as it belongs to the phenylethylamine family which provide key structural units within many pharmacological compounds^[15-19] including amphetamines as well as ingredients found in chocolate.^[20] Interestingly, whereas on its own Bu^tLi failed to sedately deprotonate DMPEA over a large temperature window instead producing the β -elimination side product styrene, the synergistic system successfully yielded greater than 95% of the metallated intermediate, which in turn could be successfully intercepted by various electrophiles in yields ranging from 74-92%. Theoretical studies probing the energetics and mechanism of this low-temperature metallation reaction suggested that both lithium and potassium participate in the transition structure of the heterometallated intermediate of DMPEA with the decisive factor in its stabilization [i.e., having a higher energy barrier to β -elimination than in the homometallated (via Bu^tLi) analogue] being the greater capacity of the large potassium cation for engaging in multihapto interactions with the negative charge delocalized over the aromatic system.



Scheme 1. Metallation of DMPEA and subsequent possible outcomes of the reaction: β -elimination generating MNMe_2 or electrophilic quenching generating an organic product.

In a recent perspective article^[21] we explained how certain alkali-metal-mediated metallation (AMMM) reactions could be interpreted as more than just the exchange of a relatively inert C–H bond for a more reactive C–M(metal) bond by a synergistic multicomponent base containing an alkali metal and usually a less electropositive metal such as magnesium or zinc. The additional factor is that following the deprotonation, because the residue of the base contains a mixture of Lewis acidic and Lewis basic coordinating sites it can capture the whole deprotonated entity intact or some fragment of it. Spectacular examples of this “cleave and capture” reactivity have come with the oxygen heterocycle THF. Upon the synergistic cleavage of it by AMMZn through a mixed lithium-zinc system,^[22] the sensitive α - C_4H_7 anion of THF has been captured and thereby stabilized, where usually it would spontaneously ring open to generate the enolate of acetaldehyde and ethene.^[23] In contrast, ring opening of THF does occur upon cleavage by AMMMg through a synergistic sodium-magnesium system but in a remarkably different way, producing a trans-but-1,3-diene dianion and an O^{2-} dianion, from a catastrophic cleavage of six of the thirteen bonds in THF.^[24] Both anions are captured by mixed-metal base residues in separate crystalline complexes.

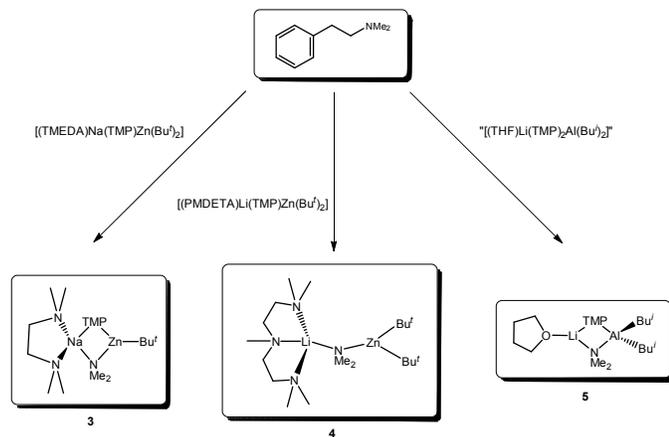
In this paper we put DMPEA under the cleave and capture chemistry spotlight. While our hope that the capturing/stabilizing capacity of mixed-metal ate systems might provide access for the first time to a β -metallated derivative of DMPEA that could be isolated and crystallographically characterized was not realized, the study still produced a number of interesting results. These include most significantly the synthesis, isolation and spectroscopic/crystallographic characterization of an organometallic compound containing intact DMPEA as a ligand. Also reported are three distinct examples of AMMM reactions where the dimethylamino (Me_2N) fragment of DMPEA has been captured by lithium-zinc, sodium-zinc or lithium-aluminium systems. Though the crystal structures of these three products of an α - β , Me_2N -metal elimination bear a close resemblance to each other, the reactions producing them appear to be mechanistically distinct. Most intriguingly, as the zinc systems follow a zincate mechanism, one can be misled into thinking that the related aluminium system follows an aluminate mechanism, when in fact a sequential lithiation/in situ alkylaluminium trapping process is in operation.

Results and discussion

AMMM reactions with DMPEA and characterization of “captured products”

Due to the success of zincate (and aluminate - see below) systems in capturing and stabilizing the cyclic α - C_4H_7 anion of THF, we opened the study by reacting DMPEA with the sodium monoamido-bisalkylzincate [(TMEDA)Na(TMP)(Bu^t Zn(Bu^t))] **1** and the related lithium zincate [(PMDETA)Li(TMP)Zn(Bu^t)₂] **2** (TMEDA is *N,N,N',N'*-tetramethylethylenediamine; TMP is 2,2,6,6-tetramethylpiperidine; PMDETA is *N,N,N',N',N'*-pentamethyldiethylenetriamine) (Scheme 2). Reagent **1** is a structurally well-defined crystalline compound^[25] and efficient metallating (zincating) agent^[26-41] [most recently with *N*-heterocyclic carbenes (NHCs)^[42] though it has occasionally also been utilized as a nucleophilic *t*-butyl source.^[43-44] Reagent **2** is a putative compound in that it has only been generated in situ by mixing LiTMP, Bu^t_2Zn , and PMDETA in a 1:1:1 ratio in hexane solution, though it is a close relation of the Kondo/Uchiyama THF-solvated reagent [(THF)Li(TMP)Zn(Bu^t)₂],^[45-49] which has been extensively studied. Our efforts focused on obtaining crystalline material suitable for X-ray crystallographic determination rather than refining reactions to get the best possible yields. While crystallization proved challenging and required prolonged storage of the reaction solutions over days, eventually both **1** and **2** afforded crystalline products from their reactions with DMPEA in [(TMEDA)Na(TMP)(NMe_2)Zn(Bu^t)] **3** and [(PMDETA)Li(NMe_2)Zn(Bu^t)₂] **4**, respectively (See Table 2 in experimental section for crystallographic data). In the case of **4** orange crystals were grown from an orange oily mixture, though NMR spectra established the mixture contained mostly

4; whereas **3** exists as a colourless crystalline solid. The formulae of **3** and **4** reveal that α - β , Me₂N-metal eliminations have taken place in both reactions with the Me₂N fragment captured in their molecular structures (note that such reactions are sometimes referred to as 1,2-eliminations and as discussed by Schlosser are highly dependent on the stereochemistry of the components of the developing new metal product formed^[50-51]).



Scheme 2. Reactions and isolated products of treating DMPEA with different bimetallic systems in hexane solutions.

Switching from zinc to aluminium, the reaction of the putative bisamido-bisalkylaluminum “[[(THF)Li(TMP)₂Al(Bu^t)₂]” (see later) with DMPEA in hexane solution follows a similar pattern to the zincate reactions producing a crystalline product with a captured Me₂N fragment in [(THF)Li(TMP)(NMe₂)Al(Bu^t)₂] **5** (Scheme 2). Though the isolated yield was only 16%, an NMR spectrum of the filtrate indicated that a lot more of the aluminate compound remained within the solution. As all three reactions were performed at ambient temperature we can surmise that the β -metallated intermediates were unstable and that the energy barriers to the α - β , Me₂N-metal eliminations are small and easily overcome at this temperature. On resorting to lower temperature in order to slow down the elimination, we found it was not possible to grow crystals of any product despite a number of attempts.

X-ray crystallographic determinations of **3** and **4** established them both to be discrete, contacted ion-pair structures (Figs. 1 and 2 respectively, with legends showing key dimensions). Sodium zincate **3** has a central four-membered (NaNZnN) ring. The three-coordinate zinc centre adopts a distorted (N₂C) trigonal planar configuration made up of two different N bridges, one from TMP, the other from NMe₂, and a terminal Bu^t group. The four-coordinate sodium occupies a distorted (4xN coordinated) tetrahedral site (with a τ_4 value of 0.65)^[52] comprising of the same amide bridges and one chelating (2xN coordinated) terminal TMEDA ligand. A search of the Cambridge Structural Database (CSD)^[53-54] (performed in December 2014, as were all the other searches mentioned in this article) returned only 4 hits for crystal structures containing a (NaNZnN) ring motif, namely

[(TMEDA)Na(NPrⁱ)₂Zn(Bu^t)],^[55]
 [(TMEDA)Na(NBu^t)₂Zn(Bu^t)],^[56]
 [(THF)₃Na{(Pr)NCH=CHN(Pr^t)}Zn(Bu^t)],^[57] and
 [(Ph₂C=NH)₂(Ph₂C=N)₄(Buⁿ)₂Na₂Zn₂].^[58] However, in all four structures the two N atoms belong to identical groups or in the case of the diazaethene the same group, indicating that **3** is a novel heteroamidozincate example. Note that a second CSD search for a Na-NMe₂-Zn fragment returned no hits.

Contrasting with the closed cyclic structure of **3**, the contact ion pair arrangement of **4** is more open with a Li-N-Zn(-C)-C chain arrangement, that branches at the Zn centre. The two metals therefore connect solely through the captured NMe₂ unit of DMPEA. This distinction with **3** is due in part to the smaller radius of lithium versus sodium and to the larger steric encumbrance and denticity (tri versus di) provided by PMDETA versus TMEDA, which prevent a second ligand gaining access into the restricted space between the two metal centres. The four-coordinate lithium occupies a distorted (4xN) tetrahedral geometry (with a τ_4 value of 0.86)^[52] made up of the bridging N(Me)₂ atom and the three PMDETA N atoms. Zinc occupies a distorted (2xC; 1xN) trigonal planar site, completed by two terminal *t*-Bu ligands. A search of the CSD uncovered only two structures featuring the Li-NMe₂-Zn chain (Fig. 3) found here in **4**, both synthesized by Hevia, with one a monoalkyl-trisamido tetraorganozincate [(TMEDA)₂Li₂ZnMe(NMe₂)₃] and the other an all-amido triorganozincate [{(TMEDA)LiZn(NMe₂)₃}₂].^[59] Significantly, however, in both these previously published structures the Li-NMe₂-Zn chain is not single stranded like that in **4**, but both metal ends join up with another atom to form a four-membered ring. Another structure bearing more similarity to **4** is the diisopropylphenylamino derivative [(PMDETA)Li(NHDipp)Zn(Me)₂]^[60] (Fig. 3), which possesses terminal PMDETA-Li and Zn(Me)₂ groups but joined by primary amino bridge.

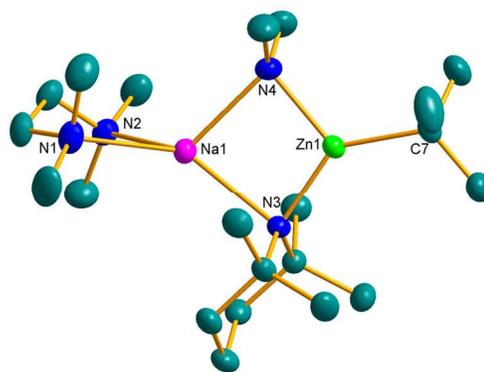


Figure 1. Molecular structure of [(TMEDA)Na(TMP)(NMe₂)Zn(Bu^t)], **3**. Ellipsoids are displayed at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Na(1)-N(4), 2.3964(14); Na(1)-N(3), 2.4480(13); Na(1)-N(1), 2.5000(14); Na(1)-N(2), 2.5314(14); Zn(1)-N(3), 1.9889(11); Zn(1)-N(4), 2.0322(13); Zn(1)-C(7), 2.0276(15); N(4)-Na(1)-N(3), 81.82(4); N(4)-Na(1)-N(1), 117.86(5); N(3)-Na(1)-N(1), 134.64(5); N(4)-Na(1)-N(2), 120.76(5); N(3)-Na(1)-N(2), 133.80(5); N(1)-Na(1)-N(2), 73.53(5); N(3)-Zn(1)-C(7), 135.41(6); N(3)-Zn(1)-N(4), 104.18(5); C(7)-Zn(1)-N(4), 120.32(6); Zn(1)-N(3)-Na(1), 86.77(4); Zn(1)-N(4)-Na(1), 87.22(5).

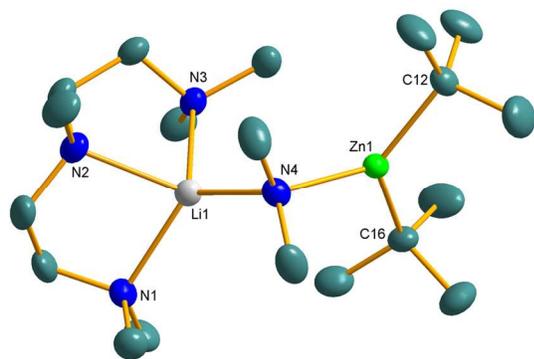


Figure 2. Molecular structure of [(PMDETA)Li(NMe₂)Zn(Bu^t)₂], **4**. Ellipsoids are displayed at 50% probability and hydrogen atoms and minor disordered component of a Bu^t arm have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Zn(1)-C(12), 2.045(2); Zn(1)-C(16), 2.048(2); Zn(1)-N(4), 2.0495(19); Li(1)-N(4), 2.050(4); Li(1)-N(3), 2.172(4); Li(1)-N(1), 2.202(4); Li(1)-N(2), 2.223(4); C(12)-Zn(1)-C(16), 125.12(10); C(12)-Zn(1)-N(4), 121.53(9); C(16)-Zn(1)-N(4), 112.94(9); N(4)-Li(1)-N(3), 113.64(19); N(4)-Li(1)-N(1), 125.5(2); N(3)-Li(1)-N(1), 115.85(19); N(4)-Li(1)-N(2), 123.01(19); N(3)-Li(1)-N(2), 84.88(16); N(1)-Li(1)-N(2), 83.02(15); Zn(1)-N(4)-Li(1), 110.63(13).

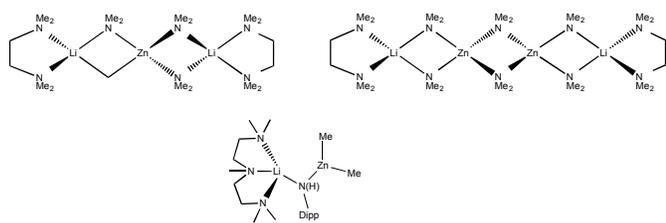


Figure 3. Molecular structures of the tetraorganozincate [(TMEDA)₂Li₂ZnMe(NMe₂)₃] and triorganozincates [(TMEDA)LiZn(NMe₂)₃]₂ and [(PMDETA)Li(NHDIpp)Zn(Me)₂].

Turning to dimensions, the bond lengths involving the sodium centre in **3** span the range 2.3964(14)-2.5314(14) Å with the bond to the small NMe₂ group [2.3964(14) Å] being the shortest. Zinc-ligand bond lengths cover the range 1.9889(11)-2.0322(13) Å, and in contrast to the sodium, the bond between the metal and the TMP anion is the shortest (by almost 0.04 Å). Summing the four endocyclic angles (360°) establishes the planarity of the (NaNZnN) ring. In comparison to the parent base [(TMEDA)Na(TMP)(Bu^t)Zn(Bu^t)], the Na-N(TMP) bond is the same length (within experimental error), whereas the Zn-N(TMP) bond is slightly shorter in **3** (but only by 0.05 Å). In **4** the three bonds involving zinc are of equal length 2.048 Å (within experimental error); whereas those around the lithium vary in size [from 2.050(4) to 2.223(4) Å], with the Li-NMe₂ bond being the shortest. The NMe₂ group sits equidistant from the Li and Zn atoms with a Li-N(4)-Zn chain angle of 110.63(13)° showing the arrangement of the three atoms is significantly bent, as opposed to linear, due to the (distorted) tetrahedral nature of the N bridge and the considerable steric bulk of the different terminal groups. The metal-NMe₂ bond lengths in **4** lie within the range of values obtained for the corresponding bonds in aforementioned [(TMEDA)₂Li₂ZnMe(NMe₂)₃] and [(TMEDA)LiZn(NMe₂)₃]₂.^[59] Having two ligand bridges

between the metal centres has a marked effect on the Li-NMe₂-Zn angle. In single stranded **4** the angle is obtuse [110.63(13)°]; whereas the corresponding angles in these TMEDA-solvated structures are acute (mean angle 80°) in order to place the metals close enough to a second ligand bridge to close the 4-membered rings.

Fig. 4 shows the molecular structure of aluminate **5** as determined by X-ray crystallography. A discrete contacted ion-pair structure, **5** bears some resemblance to zincate **3** in being heterotri-anionic and having a mixed amido ligand set (TMP and Me₂N) bridging between the two metals. This bridging arrangement gives a four-membered (LiNAIN) ring. Completed by two terminal *iso*-butyl ligands, the aluminium atom occupies a distorted (2xN; 2xC) tetrahedral site (with a τ₄ value of 0.88).^[52] The two bridging amides leave only one coordination site free for a THF molecule to complete the trigonal planar (2xN; 1xO) coordination of lithium. Aluminate **5** appears novel in the sense that it is only the second known structure containing the rare LiNAIN ring in which the two N atoms belong to different amido groups, as evidenced by a search of the CSD. Structures with the same two amido groups in a LiNAIN ring are known, the closest analogy being the bis-diisopropylamide [(THF)Li(μ-NPrⁱ)₂Al(Bu^t)₂]**5**,^[61] which also has a terminal THF ligand datively bound to lithium. The lengths of both Al-N bonds in this homoamido structure [1.935(1) and 1.936(1) Å], lie between those of the two more asymmetric Al-N bonds in heteroamido **5**, the shortest [1.9291(11) Å] to the smaller Me₂N group and the longest to the larger TMP group [1.9930(10) Å]. The asymmetry in **5** has less of an effect on the length of the Li-N bonds [2.075(3) and 2.086(3) Å; mean 2.0805 Å], with both slightly longer than the two Li-N bonds in the homoamide [1.998(2) and 2.047(2) Å; mean 2.0225 Å]. Their N-Li-N bond angles are in the same region [92.48(9)° in **5**: *cf.*, 91.45(10)°].

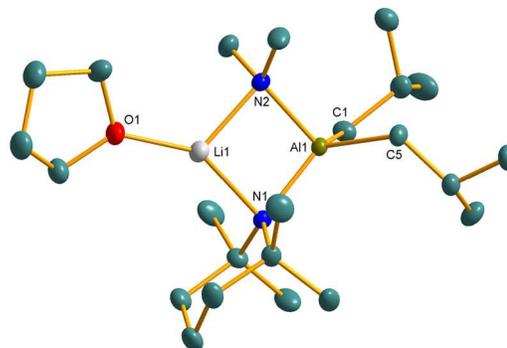


Figure 4. Molecular structure of [(THF)Li(TMP)(NMe₂)Al(Bu^t)₂], **5**. Ellipsoids are displayed at 50% probability and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al(1)-N(2), 1.9291(11); Al(1)-N(1), 1.9930(10); Al(1)-C(5), 2.0249(13); Al(1)-C(1), 2.0316(13); Li(1)-N(2), 1.998(2); Li(1)-N(1), 2.047(2); Li(1)-O(1), 1.901(2); N(2)-Al(1)-N(1), 96.32(4); N(2)-Al(1)-C(5), 106.93(5); N(1)-Al(1)-C(5), 119.87(5); N(2)-Al(1)-C(1), 109.10(5); N(1)-Al(1)-C(1), 116.51(5); C(5)-Al(1)-C(1), 106.86(6); O(1)-Li(1)-N(2), 120.96(12); O(1)-Li(1)-N(1), 146.49(13); N(2)-Li(1)-N(1), 92.48(9); Al(1)-N(2)-Li(1), 87.09(7); Al(1)-N(1)-Li(1), 84.09(7).

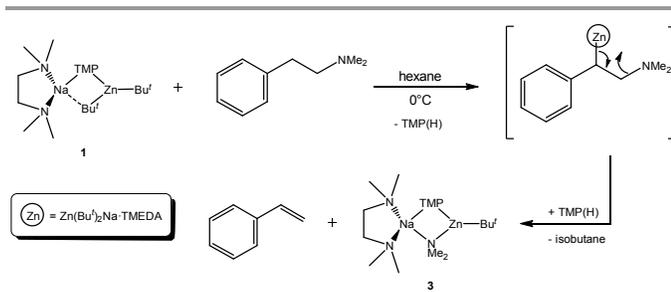
All three new compounds **3-5** were characterized in solution by NMR spectroscopy. ^1H and ^{13}C spectra of **3** recorded in d_{12} -cyclohexane solution confirmed the formula of the molecular structure identified by X-ray crystallography. A single, sharp resonance can be observed for the NMe_2 group, as well as for the terminal Bu' group. In contrast, the two sets of methyl groups on the TMP anion appear as two separate singlets, indicating that they sit in non-equivalent environments. This asymmetry is also observed for the TMP β and γ hydrogen atoms. When analyzing the ^1H NMR spectrum of the filtrate of **3** it was noticed that small resonances (at 7.28, 7.18, 6.62, 5.63 and 5.11 ppm) corresponding to styrene were present. The spectrum was compared to that of commercially available styrene, and the chemical shifts were in perfect agreement. This evidence further confirms the view that the NMe_2 fragment is a product of β -elimination from a benzylic metallated species of DMPEA since a metal dimethylamide and styrene would be the two anticipated products formed. This elimination is especially interesting as it is the reverse of a hydroamination reaction of an alkene, here styrene. Catalytic hydroamination is attracting considerable interest at present particularly apropos novel early main group catalysts.^[62-67] In addition to ^1H and ^{13}C NMR spectroscopy, lithium zincate **4** was analyzed by ^7Li NMR spectroscopy with spectra all recorded in d_{12} -cyclohexane solution. In the ^1H spectrum sharp singlets can be seen for both the Bu' and NMe_2 groups as well as the three sets of resonances expected for PMDETA. Upon drying in vacuo the crystals started to degrade to oil and therefore it was difficult to separate the pure crystalline material from impurities within the reaction mixture. As a result, resonances corresponding to free DMPEA and PMDETA were also present within the spectrum, together with small traces of styrene. The ^7Li spectrum displayed two resonances, a major one at 0.44 ppm and a minor one at 1.31 ppm, presumably from a lithium impurity arising from the aforementioned degradation of the crystals. ^1H , ^{13}C and ^7Li NMR spectra of aluminate **5** are consistent with the molecular structure determined crystallographically. Its ^1H spectrum shows a sharp singlet for the NMe_2 group implying that the two methyl groups are equivalent on the NMR timescale at room temperature, with the same being the case for the methyl TMP signals. However, both the β and γ protons on the TMP group are split, implying they experience different environments, suggesting that the TMP Me equivalency may just be a case of accidental equivalence. The ^7Li spectrum showed a narrow singlet at 1.22 ppm in agreement with a single lithium environment. Table 1 compares the chemical shifts for the NMe_2 group in each of the three heterobimetallic compounds **3-5**, as well as the ^7Li resonances in **4** and **5**. Both the ^1H and ^{13}C NMR shifts are similar for **3** and **4** in accordance that this smaller amido group is attached to zinc and an alkali metal; whereas in **5** the resonances are further upfield in comparison as it is attached to aluminium and lithium. In all of these compounds the chemical shift of the NMe_2 group is different to that of free DMPEA.

Table 1. Comparison of NMR chemical shifts (δ) of the new dimethylamide compounds in C_6D_{12} solution.

| Compound | δNMe_2 (ppm) | | $\delta ^7\text{Li}$ (ppm) |
|---|-----------------------------|-----------------|----------------------------|
| | ^1H | ^{13}C | |
| DMPEA | 2.18 | 45.72 | - |
| [(TMEDA)Na(μ -TMP)(μ - NMe_2)Zn(Bu')] (3) | 2.72 | 46.05 | - |
| [(PMDETA)Li(μ - NMe_2)Zn(Bu') ₂] (4) | 2.72 | 48.54 | 0.44 |
| [(THF)Li(μ -TMP)(μ - NMe_2)Al(Bu') ₂] (5) | 2.44 | 42.42 | 1.22 |

Mechanistic Implications

From the formulae of the products **3-5** and existing literature, interesting insights can be gained about the reactions that produced these new heterobimetallic compounds. As shown in Scheme 3, the sodium zincate starting material **1** loses one alkyl Bu' ligand that is replaced by the captured Me_2N elimination fragment in generating product **3** with retention of the rest of the structure of **1** in **3**. Though overall **1** has acted as an alkyl base with the ultimate formation of isobutane making the reaction irreversible, it is now accepted through a combination of theoretical^[47] and experimental^[68] studies that **1** performs zinc-hydrogen exchange reactions in two steps, firstly with TMP acting as a kinetic base to deprotonate the organic substrate and form amine TMP(H) co-product, which in the second thermodynamic step is deprotonated itself to regenerate TMP with release of isobutane (Scheme 3 shows this process for the conversion of **1** to **3**). Accordingly, the final product **3** ends up as a heterotri-anionic complex. Inspection of the conversion of **2** into **4** reveals a different scenario as the product **4** ends up a heterobianionic complex. In this conversion TMP executes the deprotonation of DMPEA to form TMP(H) in the first step at which point the process stops with final product **4** retaining the two *t*-butyl ligands of the starting material **2**. Dimethylamide (Me_2N^-) is significantly less basic than TMP^- (experimental $\text{p}K_a$ values of conjugate acids, 29.7 and 37.9, respectively)^[69-70] so this would rule out a transamination reaction between **4** and TMP(H), but in such terms of relative basicity one would expect TMP(H) to exchange with one of the Bu' ligands to generate hypothetical [(PMDETA)Li(NMe_2)(TMP)Zn(Bu')]. The reason this does not occur must be due predominately to steric factors. The electronic stabilization by PMDETA through its tridentate chelation fills three of the four coordination sites on the lithium cation in **4** with the fourth one filled by the small amide Me_2N , so clearly there is no space available for the TMP(H) to datively bind to Li as a prerequisite to its deprotonation by a Bu' ligand (Figure 5). The open chain arrangement within **4** is testimony to this steric restriction, whereas in both **1** and **3** the larger sodium cation only carries a terminal bidentate TMEDA which leaves room for bonding to two bridging ligands to close a 4-membered ring, so it is this steric deflation which allows TMP(H) to enter the coordination sphere of Na^+ in **1** and to then exchange with a Bu' ligand via hydrogen transfer. Drawing on the precedent of these AMMZn (zinc-hydrogen exchange) reactions, the formation of aluminate **5** could be



Scheme 3. Two-step mechanism for formation of **3** by **1** acting initially as an amido base but overall as an alkyl base.

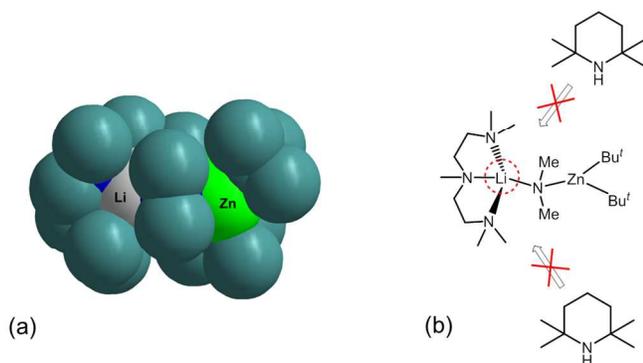
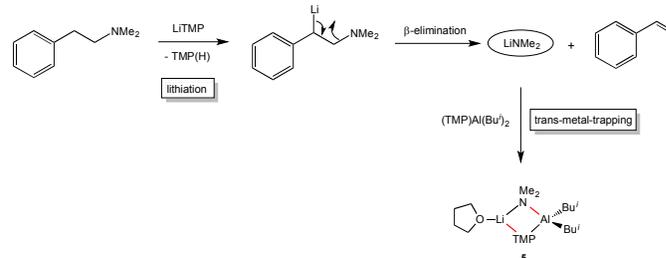


Figure 5. Space filling model (a) and ChemDraw representation (b) of **4** showing the limited space around the lithium centre preventing bulky TMP(H) re-entering the system.

considered an AMMAI (aluminium-hydrogen exchange) reaction starting from the putative contacted ion pair complex “[$(\text{THF})\text{Li}(\text{TMP})_2\text{Al}(\text{Bu}^i)_2$]”. When made in situ, this complex has previously been found to be an excellent deprotonating agent, cleaving an α -hydrogen atom from both THF and thiophene and capturing/stabilizing their sensitive anionic rings intact,^[71] regioselectively deprotonating haloanisoles without interfering with Cl, Br or I substituents,^[72] and even abstracting a hydrogen atom from the relatively non-acidic methyl terminus of the tertiary diamine TMEDA.^[73] However, while carrying out this present work, a parallel study^[74] cross-examining previous data on “[$(\text{THF})\text{Li}(\text{TMP})_2\text{Al}(\text{Bu}^i)_2$]” as well as monitoring its reaction with anisole by NMR spectroscopy (including DOSY experiments) and DFT calculations established that it exists as a separated mixture of LiTMP and $(\text{TMP})\text{Al}(\text{Bu}^i)_2(\text{THF})$. Interestingly the related base “[$(\text{THF})\text{Li}(\text{TMP})\text{Al}(\text{Bu}^i)_3$]” extensively studied by Uchiyama and Wheatley^[75-77] was analogously found not to be a single species as originally hypothesized but a complicated mixture of neutral and ate species. The surprising foremost conclusion from this parallel study was that none of the aluminium species present in these reagent mixtures, even ate species in the latter case, could deprotonate anisole under the conditions studied and that both operate as bases through a lithiation (by LiTMP) in situ *trans-metal-trapping* (by neutral aluminium species) mechanism. Moreover it was proven that in the “[$(\text{THF})\text{Li}(\text{TMP})_2\text{Al}(\text{Bu}^i)_2$]” mixture the joining together

(cocomplexation) of LiTMP and $(\text{TMP})\text{Al}(\text{Bu}^i)_2$ was forbidden on steric grounds. On the basis of this new information the probable mechanism for the production of **5** (Scheme 4) involves lithiation of DMPEA followed by α - β elimination of $\text{Me}_2\text{N-Li}$. This $\text{Me}_2\text{N-Li}$ is subsequently trans-metal-trapped by $(\text{TMP})\text{Al}(\text{Bu}^i)_2$ though it cannot be ruled out that this trapping operation occurs in a more concerted fashion with the styrene unit still attached at least partially to the departing lithium amide fragment as the trapping Al species enters the reaction. The essential point is that the reaction is not an AMMAI reaction, nor an aluminium reaction of any sort, but that the aluminium trapping agent simply cocomplexes with the eliminated $\text{Me}_2\text{N-Li}$ to form the aluminate product. Since the aluminium centre in this aluminate is coordinatively saturated (four-coordinate with bulky ligands), it is not possible for TMP(H) to react with an Al attached Bu^i ligand so there is no second step in the mechanism like that encountered in the sodium zincate reactions. This applies generally as both this mixture and “[$(\text{THF})\text{Li}(\text{TMP})\text{Al}(\text{Bu}^i)_3$]” function as TMP bases, not alkyl bases. An interesting point to note is that $(\text{Me}_2\text{N-Li})_n$ on its own is probably polymeric given lithium’s propensity for high aggregation when connected to such a small anion^[78-79] (though its crystal structure still remains elusive), but in this reaction it is never given the opportunity to aggregate which suggests the trans-metal-trapping step by the aluminium base residue occurs rapidly.



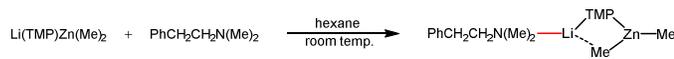
Scheme 4. Proposed mechanism of lithiation followed by trans-metal-trapping to generate **5**, highlighting the trapping Li-N and Al-N bonds.

Capture of the whole parent amine, DMPEA

Approaches for performing metallation for compounds related to DMPEA do exist whereby the nitrogen centre, otherwise capable of coordinating, is made inert and protected [for example, by using a pivaloyl (COBu^i) group]^[51], hence allowing benzylic metallation and subsequent electrophilic quenching (for example, with carbon dioxide) to be performed without any elimination competition. In the aforementioned Strohmann research, a potassium derivative of 2-*N*-methyl-1,2,3,4-tetrahydroisoquinoline, a relative of DMPEA where the tertiary amine residue resides in a ring, was synthesized and crystallographically characterized and shown to exist as a coordination polymer. However, thus far we have not managed the challenging feat of going one better by capturing a metallated derivative of DMPEA itself. That notwithstanding, as now discussed this study has been successful in unearthing a novel bimetallic complex containing intact DMPEA, that is,

without any benzylic deprotonation or subsequent Me_2N -metal elimination.

In order to try to slow down a possible benzylic deprotonation we turned to the TMP-dimethyl lithium zincate $[\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ which is less reactive than its *t*-butyl analogue $[\text{Li}(\text{TMP})\text{Zn}(\text{Bu}^t)_2]$ (as established through reactions with anisole in the presence of THF^[68]). A 1:1 reaction mixture of this reagent and DMPEA in hexane solution (Scheme 5) initially stirred at room temperature yielded upon gentle heating a homogeneous yellow solution. Storage of this solution at -28°C afforded a large crop of small colourless needles (isolated crystalline yield, 60%). Unfortunately, the crystals did not diffract well enough for their structure to be determined by X-ray crystallography, though NMR spectroscopic analysis proved possible in deuterated cyclohexane (C_6D_{12}) solution. Interestingly, the ^1H NMR spectrum revealed a 1:1 stoichiometric mixture of DMPEA and the heterobimetallic reagent $[\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ in $[\text{DMPEA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2]$ **6** establishing that both were present within the crystal structure. Whilst the results revealed that the DMPEA molecule was still intact, the corresponding resonances had all shifted downfield (to 2.38, 2.61, 2.80 and 7.08-7.18 ppm) in comparison to those in free DMPEA (2.18, 2.42, 2.68 and 7.03-7.13 ppm respectively). The ^{13}C NMR spectrum concurred with the ^1H spectrum showing resonances belonging to both TMP and $\text{Zn}(\text{Me})_2$ as well as DMPEA [though this time a upfield shift was observed for the resonances in comparison to those in free DMPEA (from 35.4, 45.7, 62.5, 126.2, 128.6, 129.1 and 141.3 ppm to 33.4, 45.5, 62.3, 126.2, 128.1, 128.2 and 138.1 ppm)]. Completing the NMR analysis, the ^7Li NMR spectrum showed a single sharp resonance at 1.89 ppm indicating only one lithium environment. These data pointed to the amine molecule interacting with the bimetallic reagent in some way, but without deprotonation having occurred, as its PhCH_2 atoms were still present. The most obvious explanation for this was a Lewis acid – Lewis base reaction between the two reagents, where the nitrogen atom of the amine coordinates datively to the Li centre. Implying that the amine part of DMPEA is the “business end” of the molecule, the shift experienced (from those in free DMPEA) by the NMe_2 hydrogen atoms is greatest (0.2 ppm) in comparison to the shift of the remote aryl group hydrogen atoms (only 0.05 ppm), though in both cases the shift differences are rather small.



Scheme 5. Suspected co-complexation reaction of $\text{Li}(\text{TMP})\text{Zn}(\text{Me})_2$ and DMPEA, highlighting the newly formed dative bond.

In view of these interesting NMR findings we repeated this reaction a number of times until we eventually managed to coax X-ray quality crystals of **6** from the reaction solution (isolated yield, 70%). Fig. 6 displays its molecular structure from two different perspectives. A key feature of this contacted $\text{LiTMP}\cdot\text{ZnMe}_2$ ion-pair structure is the central four-membered, four-

element (LiNZnC) ring. Such rings are commonly found in alkali metal zincate chemistry,^[80-81] for example in the lithium di-*t*-butylzincate $[\text{TMEDA}\cdot\text{Li}(\text{TMP})\text{Zn}(\text{Bu}^t)_2]$ ^[82] and the aforementioned dilithium methylzincate $[(\text{TMEDA})_2\cdot\text{Li}_2\text{ZnMe}(\text{NMe}_2)_3]$.^[59] However, in **6** the novel feature is the fact that a fully intact DMPEA molecule forms a Lewis acid – Lewis base complex with the ion pair through the Li centre. The three-coordinate lithium occupies a distorted ($2\times\text{N}$; $1\times\text{C}$) trigonal planar site consisting of two N atoms, one from the TMP bridge and the other from the neutral DMPEA molecule, and a C atom provided by the bridging Me group of Me_2Zn . Zn also has a three-coordinate, distorted trigonal planar ($1\times\text{N}$; $2\times\text{C}$) geometry, which is completed by a terminal Me ligand. The bridging Me group, the carbon atom of which (C11) is 5-coordinate, forms an electron deficient bridging bond to the Li centre and in turn this places the Li atom in close proximity to the methyl H atoms [$\text{Li}\cdots\text{H}(11\text{A}) = 2.18(3)$ Å, $\text{Li}\cdots\text{H}(11\text{C}) = 2.16(3)$ Å] (note that the H atoms were freely located in the X-ray diffraction analysis). The non-deprotonated DMPEA molecule coordinates to the bimetallic system through a dative nitrogen-lithium interaction, without any metallation of the amine having taken place. From Fig. 6 it is clear to see that while the N(2) atom belonging to DMPEA sits approximately in the same plane as the central $[\text{LiN}(1)\text{ZnC}]$ ring (only 0.04 Å from the mean plane), the rest of the amine molecule protrudes to one side causing the overall structure to become unsymmetrical. A search of the CSD returned no structures containing DMPEA in the presence of lithium, zinc, or indeed any metal, suggesting that compound **6** is the first of its type. Bond lengths in **6** involving lithium range from 1.965(4) - 2.248(4) Å, with the bond to the bulky TMP group being the shortest and that to the smaller methyl group being the longest. For zinc its bond lengths lie between 1.984(2) and 2.060(2) Å and in contrast, the terminal methyl group is now held closest to the metal centre (a reflection of the strong carbophilicity of Zn), while the bond to the bridging methyl group is the longest [though within experimental error of the Zn-N(TMP) bond]. The sum of the four endocyclic angles (360° within experimental error) indicates planarity of the central (LiNZnC) ring, and from Fig. 6 it is evident that this heterobimetallic ring lies essentially perpendicular to the six-membered chair-shaped TMP ring [dihedral angle between (LiNZnC) plane and the TMP $\text{C}_\alpha\text{-N-C}_\alpha$ plane is 87.45°]. To make the Li1-C11 bond the bridging methyl tilts towards the lithium atom, as evidenced by the less obtuse C11-Zn1-N1 angle [$105.25(7)^\circ$] in comparison to the significantly wider C10-Zn1-N1 bond angle [$124.85(9)^\circ$]. Comparing the Li1-C11 bond length in **6** [2.248(4) Å] with the Li-C bond lengths in methyl lithium (2.31 ± 0.05 Å)^[83-84] highlights that within experimental error the bond lengths are similar, in agreement with the Me group in **6** forming an electron deficient bond to the Li centre. However, when compared with bonds lengths in monomeric Me_2Zn ,^[85] the C-Zn bonds are shorter by 0.133 Å than that of the Zn1-C11 bond in **6**, as would be expected given the linearity of Me_2Zn and the lower coordination number of its zinc centre (i.e., CN = 2 versus 3).

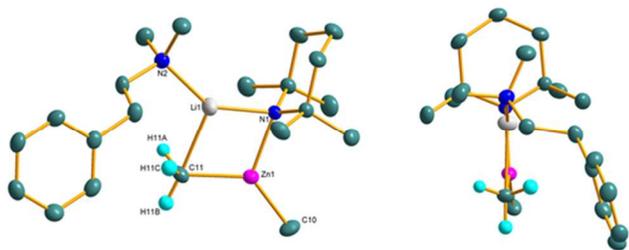


Figure 6. Molecular structure of **6** from above (LHS) and along the central LiNznc plane (RHS). Ellipsoids are displayed at 50% probability and hydrogen atoms (except those on the bridging Me group) have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Li(1)-N(1), 1.965(4); Li(1)-N(2), 2.060(4); Li(1)-C(11), 2.248(4); Li(1)-H(11A), 2.18(3); Li(1)-H(11C), 2.16(3); Zn(1)-C(10), 1.984(2); Zn(1)-N(1), 2.0520(16); Zn(1)-C(11), 2.060(2); C(10)-Zn(1)-N(1), 124.85(9); C(10)-Zn(1)-C(11), 129.87(10); N(1)-Zn(1)-C(11), 105.25(7); N(1)-Li(1)-N(2), 143.0(2); N(1)-Li(1)-C(11), 101.49(15); N(2)-Li(1)-C(11), 115.32(17); Li(1)-N(1)-Zn(1), 79.65(12); Zn(1)-C(11)-Li(1), 73.21(10).

A search of the CSD for structures containing both LiTMP and Zn(Me)₂ returned only one hit, namely the diamine complex [TMEDA·Li(TMP)Zn(Me)₂] **7**.^[86] Interestingly in **7** chelation by TMEDA to Li prevents the Me group from bridging between the two metals, resulting in a central acyclic but curved LiNznc chain (Figure 7). Whilst the Zn-N(TMP) bond length in **7** [2.0482(19) Å] is the same within experimental error as that in **6** [2.0520(16) Å], the Li-N(TMP) bond is marginally longer than in **6** (by 0.08 Å). This reflects the stronger Lewis basic bonding of TMEDA versus DMPEA. However, the most noticeable difference caused by this change of neutral donor molecule is the substantially shorter (by 0.36 Å) Li-C distance in **6** [2.248(4) Å] compared to that in **7** [2.603(5) Å], in agreement with the Me group in **6** bridging the two metal centres; while in the TMEDA compound it bonds exclusively to Zn.

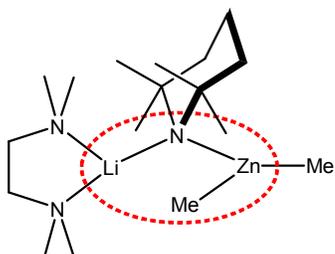


Figure 7. ChemDraw representation of acyclic TMEDA-Li(TMP)Zn(Me)₂, highlighting the curved LiNznc chain.

Donor-acceptor complex **6** was also analyzed by a combination of ¹H, ¹³C and ⁷Li NMR spectroscopy in the deuterated arene solvents benzene and toluene, as well as in the aliphatic hydrocarbon cyclohexane. In its ¹H NMR spectrum in C₆D₆ solution, the TMP methyl groups appear as two separate resonances (at 1.08 and 1.46 ppm), confirming a difference in the surrounding chemical environment for the two sets of methyl groups (note that the β and γ protons are each also split into separate resonances). That notwithstanding, in disagreement with the molecular structure is the single

resonance (at -0.24 ppm) obtained for both methyl groups present on the zinc atom. While in the crystal the interaction between Li and the Me bridge would cause an inequivalence between the methyl groups bound to zinc, in solution at room temperature there appears to be free rotation about the Zn-N(TMP) axis resulting in both groups on average experiencing the same chemical environment. This was confirmed by a variable-temperature NMR study. On decreasing the temperature from 300 K to 210 K the single resonance for the Me groups splits into two separate resonances (Figure 8), consistent with a ‘freezing out’ of the structure in solution whereby the two Me groups now sit in different environments consistent with the solid state picture established by the X-ray crystallographic studies. The ambient temperature ¹³C NMR spectrum similarly shows two distinct Me TMP resonances (located at 31.5 and 36.7 ppm) whilst only the one for those attached to zinc (located at -6.5 ppm). Though seen at different chemical shifts, the same pattern is observed for resonances of **6** in both deuterated cyclohexane and toluene solutions (see supporting information).

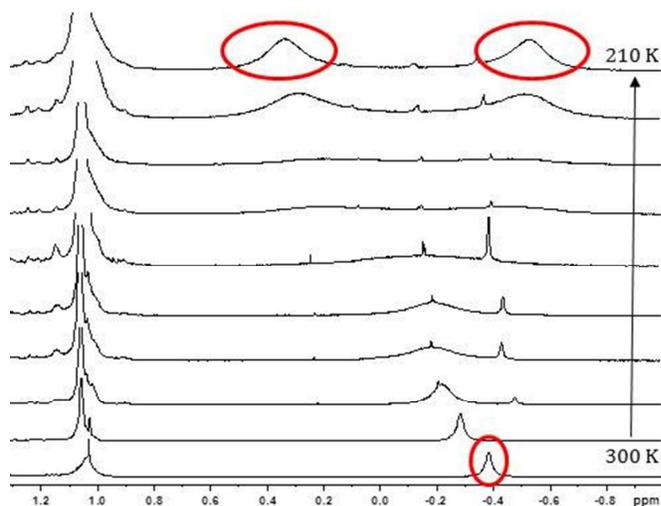


Figure 8. Variable temperature ¹H NMR study of **6** in d₈-toluene solution showing decoalescence of the Zn(Me)₂ resonance as the temperature is decreased.

Is [DMPEA·Li(TMP)Zn(Me)₂] a pre-metallation complex?

For donor-acceptor complex **6** to be considered a bona fide ‘pre-metallation complex’, metallation has to be achievable after the coordination of DMPEA to the bimetallic reagent. To ascertain if this was possible, crystals of **6** were dissolved in hexane solution and heated to reflux for eight hours. After this time, an aliquot of the solution was analyzed by ¹H NMR spectroscopy in C₆D₆ solution. While the resulting spectrum showed the trace presence of resonances corresponding to the products formed as a result of metallation followed by elimination (namely styrene at 5.05, 5.58 and 6.55 ppm and an NMe₂ fragment at 2.43 ppm) the most prominent resonances were unreacted **6**. Given that the metallation-elimination sequence of DMPEA with the sodium di-*t*-butylzincate **1** is

essentially spontaneous at 0 °C, this failure to observe any significant quantity of metallation even after a long period of heating the reaction solution to reflux seems to rule out the possibility that **6** is an intermediate en route to the cleaving of a benzylic hydrogen atom from DMPEA and the concomitant capture of the eliminated Me₂N fragment. Two possible explanations spring to mind for this lack of activity. It could be that this dimethylzincate system is just too weakly basic to deprotonate DMPEA to any significant extent; alternatively because the DMPEA molecule is tied up in a dative contact with the lithium centre it may be inaccessible for deprotonation, that is, the stereochemistry is wrong for the four-centred (NCCLi) transition state that would facilitate the elimination process. Further experiments point unequivocally towards the second explanation. For example, adding the diamine TMEDA seems to activate the zincate as mixing LiTMP, Me₂Zn, TMEDA and DMPEA in hexane solution leads to a substantial yield of crystals of the aforementioned known dilithium heterobianionic zincate [(TMEDA)₂Li₂ZnMe(NMe₂)₃], which proves a deprotonation of DMPEA must have taken place. It can be reasoned that TMEDA being the stronger donor would preferentially bind to the lithium and thus free up the DMPEA for its intermolecular deprotonation. Moreover, taking crystals of **6** and dissolving them in bulk THF and monitoring the solution by ¹H NMR studies revealed the disappearance of DMPEA resonances and the emergence of a Me₂N resonance, consistent with a reaction mimicking that involving TMEDA.

Experimental

General Methods

All reactions and manipulations were carried out under a protective dry pure argon atmosphere using standard Schlenk techniques. Products were isolated and NMR samples prepared within an argon-filled glovebox. Hexane was dried by heating to reflux over sodium-benzophenone and distilled under nitrogen prior to use. BuⁿLi (1.6 M in hexanes), ZnMe₂ (1.0 M in heptane) and BuⁿLiAlCl₂ were purchased from Aldrich and used as received. TMP(H) was obtained from Aldrich and dried over 4 Å molecular sieves prior to use. TMEDA, PMDETA and DMPEA were distilled over CaH₂ and stored over 4 Å molecular sieves prior to use. ZnCl₂ was purchased from Aldrich and dried under vacuum prior to use. ZnBu₂ was prepared and isolated according to a standard literature procedure.^[25] Zn(TMP)₂ was prepared and isolated according to a modified literature method (see supporting information).^[87] NMR spectra were recorded on a Bruker AVANCE 400 NMR spectrometer, operating at 400.13 MHz for ¹H, 155.50 MHz for ⁷Li and 100.62 MHz for ¹³C. All ¹³C NMR spectra were proton decoupled. ¹H and ¹³C spectra were referenced to the appropriate solvent signal and ⁷Li NMR spectra were referenced against LiCl in D₂O at 0.00 ppm. Note that despite repeated attempts the elemental analyses (C, H, N) determined for the NMe₂-containing complexes **3-5** proved inconsistent. In the case of **4** this was due presumably to the presence of an

unidentified oily impurity. Complex **6** on the other hand gave a satisfactory analysis. These were all carried out on a Perkin-Elmer 2400 elemental analyser.

Crystal structure determinations

Crystallographic data were collected at 123(2) K on Oxford Diffraction Diffractometers with MoK_α (λ=0.71073 Å) or CuK_α (λ=1.54180 Å) radiation. Structures were solved using SHELXS-97, and refined to convergence on F² against all independent reflections by the full-matrix least-squares method using the SHELXL-97 program.^[88] Raw data for complex **6** was processed as twinned to give a hklf 5 formatted file. Twin matrix used was -1 0 0 0 -1 0 0.73 0 1. The contribution of the second crystal (as BASF) was refined to 0.2911(8). Using the data processed in this manner gave improvements to the model in terms of R factors and residual Q peaks (when compared to a refinement with hklf 4 formatted data and no twin processing). CCDC-1042454, CCDC-1042455, CCDC-1042456 and CCDC-1042457 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)(NMe₂)Zn(Buⁿ)], **3:** The sodium zincate starting material [(TMEDA)Na(μ-TMP)(μ-Buⁿ)Zn(Buⁿ)] was prepared according to the standard literature procedure^[25] and isolated in crystalline form. To an oven-dried Schlenk tube was added [(TMEDA)Na(μ-TMP)(μ-Buⁿ)Zn(Buⁿ)] (0.46 g, 1 mmol) which was dissolved (with heating) in 10 mL of hexane to give a pale yellow solution. The flask was then cooled to 0°C and immediately *N,N*-dimethylphenylethylamine (0.17 mL, 1 mmol) was introduced. This resulted in the precipitation of a solid. The flask was then placed into the refrigerator (at 5°C) and after a few days a crop of colourless crystals of **3** had formed in solution (0.08 g, 18% yield). ¹H NMR (C₆D₁₂, 400.03 MHz, 300K) δ = 2.72 (s, 6H, NMe₂), 2.32 (s, 4H, CH₂, TMEDA), 2.22 (s, 12H, CH₃, TMEDA), 1.75 (m, 1H, γ-TMP), 1.67 (m, 1H, γ-TMP), 1.48 (m, 2H, β-TMP), 1.14 (s, 6H, CH₃, TMP), 1.10 (m, 2H, β-TMP), 1.05 (s, 9H, Buⁿ), 1.03 ppm (s, 6H, CH₃, TMP); ¹³C {¹H} NMR (C₆D₁₂, 100.60 MHz, 300K) δ = 58.2 (CH₂, TMEDA), 52.4 (α-TMP), 47.0 (NMe₂), 46.4 (CH₃, TMEDA), 41.0 (β-TMP), 36.8 (CH₃, TMP), 35.10 (CH₃, TMP), 35.0 (CH₃, Buⁿ), 22.9 (Buⁿ quaternary), 20.5 ppm (γ-TMP).

Synthesis of [(PMDETA)Li(NMe₂)Zn(Buⁿ)₂], **4:** The lithium di-*t*-butyl zincate compound [(PMDETA)Li(TMP)Zn(Buⁿ)₂] was first prepared *in situ* before *N,N*-dimethylphenylethylamine was added. A solution of Buⁿ₂Zn (0.36 g, 2 mmol) in hexane (10 mL) was transferred via a cannula into a separate Schlenk tube containing a freshly prepared solution of LiTMP in hexane (10 mL) [prepared from a mixture of BuⁿLi (1.6 M in hexane, 1.25 mL, 2 mmol) and TMP(H) (0.34 mL, 2 mmol)]. The resulting colourless solution was allowed to stir for 10 minutes before PMDETA (0.42 mL, 2 mmol) was injected into it, producing a yellow oil-like substance within the flask. *N,N*-

Table 2. Crystallographic data and refinement details for compounds 3-6.

| Compound | 3 | 4 | 5 | 6 |
|---|---|---|--|---|
| Formula | C ₂₁ H ₄₉ N ₄ NaZn | C ₁₉ H ₄₇ N ₄ LiZn | C ₂₃ H ₅₀ N ₅ OLiAl | C ₂₁ H ₃₉ N ₂ LiZn |
| Formula weight | 446.00 | 403.92 | 404.57 | 391.85 |
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic | Monoclinic |
| Space group | P bca | P bcn | P 21/n | P 21/n |
| Wavelength/Å | 1.54180 | 0.71073 | 0.71073 | 1.54180 |
| a/Å | 15.4328(3) | 29.1528(10) | 13.5126(9) | 10.3686(2) |
| b/Å | 18.1148(3) | 9.1827(3) | 12.4361(8) | 9.9831(2) |
| c/Å | 18.7053(3) | 18.4451(6) | 15.2536(10) | 21.6606(4) |
| α° | 90 | 90 | 90 | 90 |
| β° | 90 | 90 | 91.834(6) | 100.177(2) |
| γ° | 90 | 90 | 90 | 90 |
| Volume/Å ³ | 5229.29(16) | 4937.8(3) | 2562.0(3) | 2206.83(7) |
| Z | 8 | 8 | 4 | 4 |
| Refls. collected | 5215 | 5914 | 6517 | 10745 |
| 2θ _{max} | 72.94 | 28.7470 | 29.4143 | 72.9589 |
| R _{int} | 0.0292 | 0.0573 | 0.0303 | |
| Goodness of fit | 1.093 | 1.021 | 1.029 | 1.086 |
| R[F ² > 2σ], F | 0.0348 | 0.0457 | 0.0419 | 0.0498 |
| R _w (all data), F ² | 0.0959 | 0.1026 | 0.1132 | 0.1594 |

Dimethylphenylethylamine (0.34 mL, 2 mmol) was then added and the flask moved to the freezer (at -28°C) for storage. After a few weeks, small star-shaped orange crystals of **4** had formed on an orange oily substance present in the bottom of the Schlenk tube (a yield was unattainable). ¹H NMR (C₆D₁₂, 400.03 MHz, 300K) δ = 2.72 (s, 6H, NMe₂), 2.37 (s, 3H, NMe, PMDETA), 2.34 (bs, 8H, CH₂, PMDETA), 2.29 (s, 12H, NMe₂, PMDETA), 1.01 ppm (s, 18H, Bu^t₂Zn); ¹³C {¹H} NMR (C₆D₁₂, 100.60 MHz, 300K) δ = 58.7 (CH₂, PMDETA), 48.5 (NMe₂), 46.6 (NMe₂, PMDETA), 46.5 (NMe, PMDETA), 35.3 ppm (Bu^t₂Zn); ⁷Li (C₆D₁₂, 155.50 MHz, 300K) δ = 0.44 ppm(s), with an unidentified smaller signal at 1.31 ppm.

Synthesis of [(THF)Li(TMP)(NMe₂)Al(Bu^t)₂], **5:** In an oven-dried Schlenk tube the bimetallic mixture “[[(THF)Li(TMP)₂Al(Bu^t)₂]” was prepared *in situ* (in a hexane solution) according to a literature method.^[71] *N,N*-dimethylphenylethylamine (0.17 mL, 1 mmol) was then added and the reaction mixture allowed to stir for 10 minutes. The solution was then concentrated to half the volume by removing some solvent *in vacuo* and the flask transferred to the freezer (at -69°C). A crop of colourless crystals of **5** was deposited after a few weeks storage (0.07 g, 16% yield). ¹H NMR (C₆D₁₂, 400.03 MHz, 300K) δ = 3.89 (m, 4H, OCH₂, THF), 2.44 (s, 6H, NMe₂), 2.01 (m, 2H, CH, Bu^t), 1.96 (m, 4H, CH₂, THF), 1.90 (bs, 1H, γ-TMP), 1.60 (bs, 2H, β-TMP), 1.45 (bs, 1H, γ-TMP), 1.32 (s, 12H, CH₃, TMP), 0.99 (m, 12H, CH₃, Bu^t), 0.91 (bs, 2H, β-TMP), 0.18 ppm (m, 4H, CH₂, Bu^t); ¹³C {¹H} NMR (C₆D₁₂, 100.60 MHz, 300K) δ = 69.7 (OCH₂, THF), 52.2 (α-TMP), 45.9 (β-TMP), 42.4 (NMe₂), 30.0 (overlapping CH₃-TMP and CH₃, Bu^t), 29.3 (CH₂, Bu^t), 28.0 (CH₃, Bu^t), 27.8 (CH, Bu^t), 26.0 [CH₂, THF (under solvent peak)], 19.0 ppm (γ-TMP); ⁷Li (C₆D₁₂, 155.50 MHz, 300K) δ = 1.22 ppm (s).

Synthesis of [DMPEA·Li(TMP)Zn(Me)₂], **6:** Me₂Zn (1.0 M in heptane, 2 mL, 2 mmol) was delivered dropwise to a freshly prepared solution of LiTMP in hexane (10 mL) [prepared from a mixture of BuⁿLi (1.6 M in hexane, 1.25 mL, 2 mmol) and TMP(H) (0.34 mL, 2 mmol)] resulting in the immediate precipitation of a white solid. *N,N*-Dimethylphenylethylamine (0.34 mL, 2 mmol) was then added resulting in the dissolution of the white solid to give a homogeneous yellow solution. After a couple of minutes stirring a white solid precipitated from solution which upon gentle heating dissolved to give again a homogeneous solution. The Schlenk tube was then placed in a Dewar flask of hot water and allowed to cool to room temperature. Storage of the solution overnight in the freezer (at -28°C) provided a crop of white needles of **6** [0.56 g, 71% yield] which were suitable for X-ray crystallographic analysis. ¹H NMR (C₆D₆, 400.03 MHz, 300 K): δ=7.15 (m, 2H, H_{meta}, DMPEA), 7.08 (m, 1H, H_{para}, DMPEA), 7.00 (m, 2H, H_{ortho}, DMPEA), 2.51 (m, 2H, NCH₂, DMPEA), 2.22 (m, 2H, PhCH₂, DMPEA), 1.94 (bs, 1H, γ-TMP), 1.82 (s, 6H, NMe₂, DMPEA), 1.73 (bs, 1H, γ-TMP), 1.65 (bs, 2H, β-TMP), 1.46 (s, 6H, CH₃, TMP), 1.13 (bs, 2H, β-TMP), 1.08 (s, 6H, CH₃, TMP), -0.24 ppm (s, 6H, Me₂Zn); ¹³C NMR (C₆D₆, 100.60 MHz, 300 K) δ=138.9 (C_{ipso}, DMPEA), 128.9 (C_{meta}, DMPEA), 128.8 (C_{ortho}, DMPEA), 126.8 (C_{para}, DMPEA), 62.0 (NCH₂, DMPEA), 53.4 (α-TMP), 45.5 (NMe₂, DMPEA), 41.1 (β-TMP), 36.7 (CH₃, TMP), 33.5 (PhCH₂, DMPEA), 31.5 (CH₃, TMP), 20.0 (γ-TMP), -6.5 ppm (Me₂Zn); ⁷Li (C₆D₆, 155.50MHz, 300 K) δ=1.55 ppm (s). Elemental analysis calc (%): C 64.35, H 10.03, N 7.15; found: C 64.22, H 10.16, N 7.41.

Conclusions

This study has extended the idea of cleave and capture chemistry to the important bio-relevant scaffold DMPEA.

Cleavage of a benzylic CH bond is followed by the elimination and capture of a Me₂N fragment by bimetallic Na-Zn, Li-Zn or Li-Al capturing agents. Interestingly, it does not appear to matter whether the initial base operates in a *synergic synchronized* style (as in **1** and **2**), where the two metals work side-by-side in the same molecule, or in a *synergistic stepwise* style [as in “{(THF)Li(TMP)₂Al(Bu^t)₂}” = LiTMP and (TMP)Al(Bu^t)₂-THF], where the two metals work in tandem but in separate species, as in each case following the deprotonation the Me₂N fragment is captured. Though DMPEA could be captured intact by the weakly basic dimethylzincate reagent [Li(TMP)Zn(Me)₂] in a Lewis acid – Lewis base complex, a metallated intermediate of DMPEA prior to the α-β elimination proved elusive. Future work will focus on utilizing these and related heterobimetallic bases as storage vehicles for other sensitive ions formed by deprotonation events, so enabling the controlled transportation of these ions to other sites in subsequent syntheses.

Acknowledgements

We gratefully acknowledge the generous support of the Royal Society (Wolfson Merit Award to R.E.M.), the Royal Society of Edinburgh (BP Trust Fellowship to S.D.R.), the European Research Council (ERC Starting Grant to E.H.), and the University of Strathclyde/EPSCRC (Doctoral Training Grant to D.L.R.). Our colleagues Prof E. Hevia and Dr C. O’Hara are also thanked for their useful advice on many different aspects of the work as well as Dr M. Ángeles Fuentes for her help with the microanalysis.

Notes and references

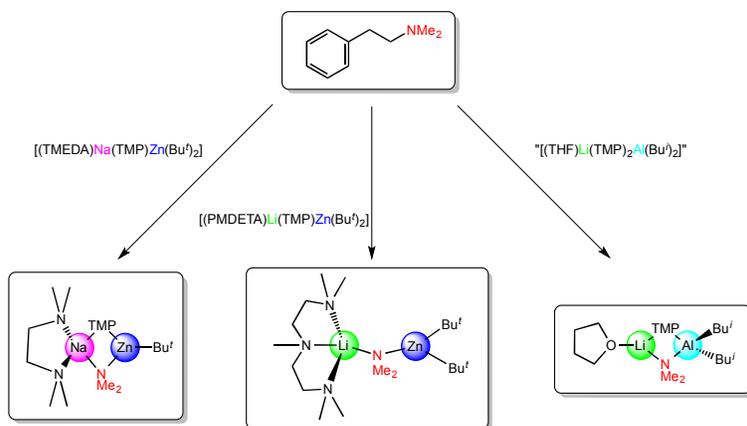
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† Dedicated to the memory of Ken Wade FRS. Friend, mentor and inspiration to R.E.M.

Electronic Supplementary Information (ESI) available: NMR spectroscopic data and X-ray data in crystallographic file (CIF) format for compounds **3**, **4**, **5** and **6**. CCDC reference numbers 1042454 – 1042457. See DOI: 10.1039/b000000x/

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The cleave and capture capacity of various bimetallic amido-alkyl mixtures is illustrated through reaction with the deprotonation sensitive *N,N*-dimethylphenylethylamine