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Synthetic and Reactivity Studies of Hetero-tri-anionic Sodium Zincates

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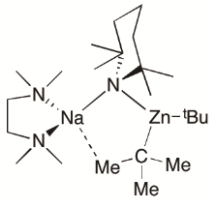
The synthesis and characterisation of several sodium zincate complexes is reported. The all-alkyl monomeric sodium zincate (PMEDTA)·Na(μ-CH_2SiMe_3)Zn^{t}Bu$_2$ **2**, is prepared by combining an equimolar quantity of ^{t}Bu$_2$Zn, ^{n}BuNa and PMDETA (*N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine)]. A similar approach was used to prepare and isolate the unusual dimeric zincate [(PMEDTA)·Na(μ-^{n}Bu)Zn^{t}Bu$_2$]$_2$ **3**. When an equimolar mixture of ^{n}BuNa, ^{t}Bu$_2$Zn and TMP(H) (2,2,6,6-tetramethylpiperidine) are combined in hexane, the hetero-tri-leptic TMP(H)-solvated zincate (TMPH)Na(μ-TMP)(μ-^{n}Bu)Zn^{t}Bu **4** was forthcoming. Complex **4** can also be prepared using a rational approach [*i.e.*, utilising two molar equivalents of TMP(H)]. When TMEDA is reacted with an equimolar mixture of ^{n}BuNa, ^{t}Bu$_2$Zn and TMP(H), the monomeric sodium zincate (TMEDA)Na(μ-TMP)(μ-^{n}Bu)Zn^{t}Bu **5** was obtained – this complex is structurally similar to the synthetically useful relation TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu) **1**. By changing the sodium reagent used in the synthesis of **5**, it was possible to prepare (TMEDA)Na(μ-TMP)(μ-Me_3SiCH_2)Zn^{t}Bu **6**. By reacting **5** with *cis*-DMP(H) (*cis*-2,6-dimethylpiperidine), the zincate could thermodynamically function as a amide base, to give the transamination product (TMEDA)Na(μ-*cis*-DMP)(μ-^{n}Bu)Zn^{t}Bu **7**, although no crystals could be grown. However, when HMDS(H) (1,1,1,3,3,3-hexamethyldisilazane) or PEA(H) [(+)-*bis*[(*R*)-1-phenylethyl]amine] is reacted with **5**, crystalline (TMEDA)Na(μ-HMDS)(μ-^{n}Bu)Zn^{t}Bu **8** or (TMEDA)Na(μ-PEA)(μ-^{n}Bu)Zn^{t}Bu **9** are isolated respectively. With PNA(H) (*N*-phenylnaphthalen-1-amine) the reaction took a different course and resulted in the formation of the dimeric sodium amide complex [(TMEDA)Na(PNA)]$_2$ **10**. When reacted with benzene, it appears that a TMEDA-free variant of **5** functions thermodyanically as an ^{n}Bu base to yield the previously reported (TMEDA)Na(μ-TMP)(^{t}Bu)Zn(μ-C_6H_4)Zn(^{t}Bu)(μ-TMP)Na(TMEDA) **11**. Finally when reacted with TEMPO (2,2,6,6-tetramethylpiperidinyloxy), **5** undergoes a single electron transfer reaction to form (TMEDA)Na(μ-TMP)(μ-TEMPO)Zn^{n}Bu **12**.

Introduction

Since the turn of the millennium, alkali metal ate complexes (where an alkali metal organometallic reagent is combined with another less polar organometallic reagent) have come to the fore in synthetic chemistry.[1-6] This interest is primarily due to the fact that mixed metal species can often perform chemistry, which is unobtainable by the monometallic constituent parts, or it can be utilized at more user-friendly reaction temperatures and in the presence of donor solvents or reactive functional groups. TMP-ate complexes (where TMP is 2,2,6,6-tetramethylpiperidide), particular magnesiate[7-24] and zincate reagents[25-30] are amongst the most widely studied. Focusing on TMP-zincate systems, several donor-solvated heterobimetallic formulations have been crystallographically-characterized including (TMEDA)·Li(μ-TMP)(μ-^{n}Bu)Zn(^{n}Bu),[31] (TMEDA)·Li(μ-TMP)Zn(Me)$_2$,[32] (THF)·Li(μ-TMP)Zn(^{t}Bu)$_2$,[30, 33-35] (TMEDA)·Na(μ-TMP)(μ-CH_2SiMe_3)Zn(CH_2SiMe_3)[36] and most pertinent to this study (TMEDA)·Na(μ-TMP)(μ-^{t}Bu)Zn(^{t}Bu) **1**.[37]



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Sodium zincate **1**, can act as a powerful base, regioselectively deprotonating arenes, heterocycles, and metallocenes.[37-40] It can also act as a source of a *t*-butyl group, where the zincate formally adds across ketones in an unusual 1,6-manner.[41, 42] We also discovered that **1** can undergo single electron transfer (SET) with the stable oxy-radical TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] and chalcone (PhCOCH=CHPh).[43] In this work, the synthesis of TMP-zincates is probed and a series of hetero-tri-leptic zincates (*i.e.*, species that contain three different anionic ligands) is prepared. Finally, the reactivity of a prototypical zincate towards deprotonation, addition, SET and amide exchange reactions is studied.

Results and Discussion

RNa

R = Me_3Si

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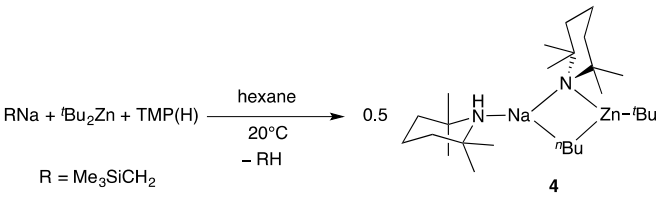
Syntheses and NMR Spectroscopic Characterization of sodium zincates 2-6

The first objective of this study was to probe further the synthesis of TMP-sodium zincates. As mentioned in the introduction, previous work has focused on the synthesis and reactivity of **1**.[37] Sodium zincate **1** is formed via co-complexation of a 1:1:1 stoichiometric mixture of NaTMP (itself preformed via a reaction between ^{n}BuNa and TMPH), ^{t}Bu$_2$Zn and TMEDA. In this work, a 1:1 mixture of the alkyl reagents ^{n}BuNa and ^{t}Bu$_2$Zn was studied. On addition of freshly prepared hexane solution of ^{t}Bu$_2$Zn to the white suspension of ^{n}BuNa in hexane, surprisingly immediate dissolution occurred. ^{1}H NMR spectroscopic analysis of this mixture in a *cyc*-C_6D_{12} solution, revealed the expected *n*- and *tert*-butyl resonances. Relying on these data, it was not immediately obvious that co-complexation had occurred as the chemical shift associated with the ^{t}Bu group was identical to that of ^{t}Bu$_2$Zn (1.09 ppm); however, there is an ^{n}Bu CH_2 resonance at −0.79 ppm (integrating to two H atoms, with respect to 18 for the ^{t}Bu H atoms). A perfect solution was obtained, suggesting that the insoluble monometallic starting material ^{n}BuNa[44] (or indeed the potential metathetical product, ^{t}BuNa) was not present in the mixture. Unfortunately, all attempts to obtain suitable X-ray quality crystals from this mixture were unsuccessful. Therefore, in an effort to shed some structural insight into the complexation of sodium and zinc alkyl reagents, we exchanged ^{n}BuNa for (trimethylsilyl)methylsodium (Me$_3$SiCH$_2$Na).[45, 46] The trimethylsilyl)methyl anion was chosen as it aids stability (due to the lack of β–hydrogen atoms), solubility and is known to crystallize well when it is a component of s-block metal complexes.[45, 47-53] Unfortunately, again no crystalline material was forthcoming so a donor ligand was introduced [namely the tridentate amine PMDETA (*N*,*N*′,*N*′′,*N*′′′-pentamethyldiethylenetriamine)]. When a 1:1:1 mixture of Me$_3$SiCH$_2$Na, ^{t}Bu$_2$Zn and PMDETA was combined in hydrocarbon solution a white solid formed, which was easily dissolved by gentle heating. Storing this solution at −28 °C resulted in the formation of colourless crystals (in 61% non-optimized yield). X-ray diffraction analysis (vide infra) revealed the formation of the all-alkyl monomeric sodium zincate (PMEDTA)·Na(μ-CH$_2$SiMe$_3$)Zn^{t}Bu$_2$ **2** (Scheme 1). A similar approach was ultimately used to prepare and isolate the dimeric [(PMEDTA)·Na(μ-^{n}Bu)Zn^{t}Bu$_2$]$_2$ **3**. NMR spectroscopic analysis of *cyc*-C_6D_{12} solutions of crystalline **2** and **3** at 300K appeared to confirm the three different anions in each of the complexes were present in a 1:1:1 ratio, and that only one type of each was present, therefore suggesting that no ligand scrambling was occurring.

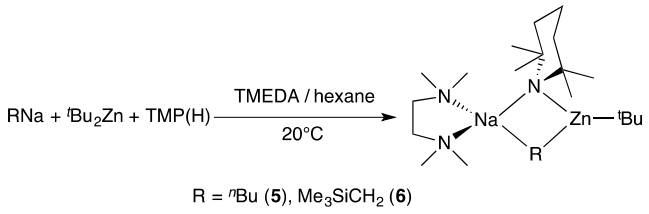
Scheme 1. Syntheses of PMEDTA-solvated *tris*(alkyl)sodium zincates **2** and **3**.

The next step in this study, was to ascertain the reactivity of a hydrocarbon solution of the donor-free variant of **3** [*i.e.*, 'Na(^{n}Bu)Zn^{t}Bu$_2$'] with the secondary amine TMP(H). In this reaction, an equimolar mixture of ^{n}BuNa and ^{t}Bu$_2$Zn in hexane was stirred for 30 minutes (Scheme 2). One equivalent of TMP(H) was then added via syringe, before allowing the solution to stir for 1 hour, before cooling to −28°C. This resulted in the crystallization of the hetero-tri-leptic TMP(H)-solvated zincate (TMPH)Na(μ-TMP)(μ-^{n}Bu)Zn^{t}Bu **4** in 66% yield [based on TMP(H) consumption]. The incorporation of TMP(H) as a donor ligand is unusual but has been observed previously in a sodium-magnesium ferrocenophane complex.[54] Complex **4** may be viewed as a precursor to a bis(TMP) zincate; however, thus far we have not been able to activate the relatively acidic amino-NH by heating aliphatic hydrocarbon or arene solutions of **4**. Complex **4** can also be prepared rationally by introducing two equivalents of TMP(H) to the sodium-zinc tris(alkyl) mixture.



Scheme 2. Initial synthetic route to **4**. Note that it can also be prepared in a rational manner by employing two equivalents of TMP(H).

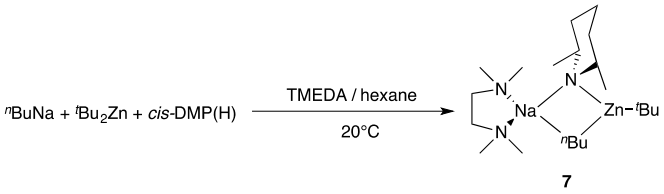
When TMEDA is added to a 1:1:1 mixture of ^{n}BuNa, ^{t}Bu$_2$Zn and TMP(H) in hexane, a white precipitate which was easily dissolved by gentle heating, and subsequent cooling at −28°C yielded crystals of (TMEDA)Na(μ-TMP)(μ-^{n}Bu)Zn^{t}Bu **5** in good yield (60%). Following a similar procedure, when TMEDA is added to a 1:1:1 mixture of Me$_3$SiCH$_2$Na, ^{t}Bu$_2$Zn and TMP(H), gently heated, and cooled to −28°C crystals of (TMEDA)Na(μ-TMP)(μ-Me$_3$SiCH$_2$)Zn^{t}Bu **6** (Scheme 3) deposited in good yield (61%). The NMR spectroscopic data for **5** and **6** in *cyc*-C_6D_{12} solution (Table 1) show the expected 1:1:1 ratio of anionic ligands and that the respective donor ligand remains attached to the metal at 300 K. At this juncture, the incorporation of other amines [*i.e.*, other than TMP(H)] into the zincates was investigated.



Scheme 3. Synthesis of TMEDA-solvates **5** and **6**.

The first alternative amine which was examined was 2,6-*cis*-dimethylpiperidine, *cis*-DMP(H). This amine has recently been used to prepare ate reagents[55] which have been utilized in deprotonation reactions.[56] From a synthetic-viability viewpoint,

it is considerably less expensive than TMP(H).[57] When it was used in place of TMP(H) (*i.e.*, in the synthesis of **5**) it was expected that a zincate with empirical formula (TMEDA)Na(μ-*cis*-DMP)(μ-^{n}Bu)Zn^{t}Bu **7** could be isolated (Scheme 4). However, no high quality crystalline material could be obtained. NMR spectroscopic data revealed that signal for a *cis*-DMP, ^{t}Bu, TMEDA and ^{n}Bu ligands were all evident. Table 1 contains a summary of the NMR spectroscopic data for the alkyl ligands present in **2**-**7**. These data suggest that the respective ^{1}H and ^{13}C NMR spectroscopic resonances for the ZnCH_2 and the Zn^{t}Bu groups in **5** and **7** have similar chemical shifts [−0.42 *vs* −0.40; 1.05 *vs* 1.01; 16.6 *vs* 15.9; 34.0 *vs* 34.1], providing evidence that a similar structural framework exists when either *cis*-DMP or TMP is employed. Complex **5** can be viewed as a closely related, tri-heteroleptic mimic of **1**, as such it was decided to explore the reactivity of **5** with a host of important organic substrates which are known to react with **1**.



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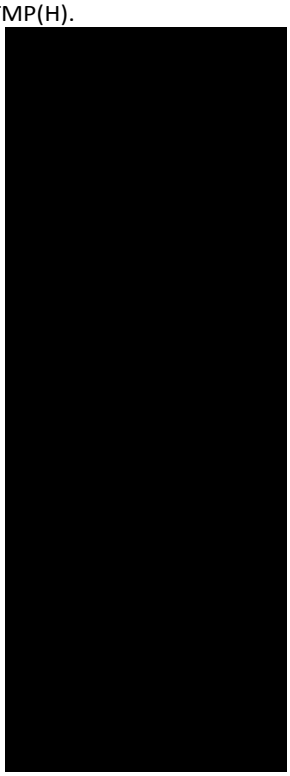
Scheme 4. Synthesis of *cis*-DMP zincate **7**.

Table 1. ^{1}H and ^{13}C NMR chemical shifts (ppm) of ^{t}Bu$_2$Zn, NaZn^{t}Bu$_2^n$Bu, NaZn^{t}Bu$_2$(CH$_2$SiMe$_3$) and zincates (**2-7**) performed in *cyc*-C_6D_{12} at 293 K (400 MHz).

Compound	δ(^{1}H) $ZnCH_2$	δ(^{1}H) ^{t}Bu	δ(^{13}C) $ZnCH_2$	δ(^{13}C) ^{t}Bu
^{t}Bu$_2$Zn		1.09		30.12
^{t}Bu$_2^n$BuNaZn	−0.20	1.09	10.28	30.79
^{t}Bu$_2$(CH$_2$SiMe$_3$)NaZn	−1.35	1.10	−1.21	31.58
2	−1.36	1.02	−3.08	33.53
3	−0.13	1.05	12.06	33.55
4	−0.32	1.06	16.56	30.18
5	−0.42	1.05	16.62	33.98
6	−1.42	1.03	−0.78	35.38
7	−0.40	1.01	15.92	34.08

Exploring the synthetic utility of sodium zincate 5

The remainder of the synthetic work in this paper focuses on the reactivity of **5**. Firstly, by treating a hexane solution of **5** with an equimolar quantity of 1,1,1,3,3,3-hexamethyldisilazane [HMDS(H)], **5** undergoes a transamination reaction [with concomitant loss of TMP(H)] to form (TMEDA)Na(μ-HMDS)(μ-^{n}Bu)Zn^{t}Bu **8** in 45% non-optimised yield (Scheme 5). In this instance **5** is formally acting as an amido-base. A transamination reaction was also observed when **1** is utilised;[58] however, unlike **8**, a solvent-separated ion pair structure was the major product [{(TMEDA)$_2$Na}$^+${Zn(^{t}Bu)$_2$(HMDS)}$^-$]. The addition of excess TMEDA, in an attempt to drive **8** to a solvent-separated system failed; hence, it seems clear that the structural difference observed between **8** and [{(TMEDA)$_2$Na}$^+${Zn(^{t}Bu)$_2$(HMDS)}$^-$][58] is due to the steric difference between the ^{t}Bu/^{n}Bu arrangement versus the ^{t}Bu/^{t}Bu one. When **5** is reacted with an equimolar quantity of the chiral secondary amine (+)-*bis*[(*R*)-1-phenylethyl]amine [PEA(H)] in hexane solution, again the zincate formally acts as an amido base to yield (TMEDA)Na(μ-PEA)(μ-^{n}Bu)Zn^{t}Bu **9** (that can be isolated as colourless crystals in a 48% yield) and TMP(H).



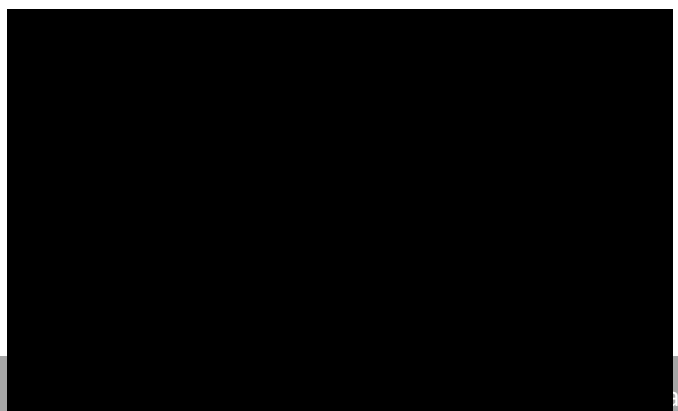
Scheme 5. Transamination reaction of **5** with HMDS(H) or PEA(H) to produce **8** or **9** respectively.

Complex **5** was also reacted with one molar equivalent of *N*-phenylnaphthalen-1-amine [PNA(H)] in hexane. Due to solubility issues (which were not encountered in any of the previously discussed reactions), it seemed clear that the reaction had taken a different/unexpected route. The yellow precipitate which was obtained could not be dissolved in hexane and was only partially soluble in benzene or toluene solution. ^{1}H NMR spectroscopic analysis of a C_6D_6 solution of this solid only revealed resonances corresponding to the H atoms of a PNA ligand and TMEDA, in a 3:4 ratio. Addition of THF to a benzene solution of the solid, followed by gentle warming produced homogeneity. Crystallization at ambient temperature, yielded yellow crystals of the TMEDA-solvated sodium amide [(TMEDA)Na(PNA)]$_2$ **10** (Scheme 6). The unexpected synthesis of this sodium-only product, suggests that a zincate redistribution is taking place when PNA(H) is added to **5**. Stoichiometrically, it would be expected that the zinc-containing by-product from this reaction could be: (i) ^{t}Bu^{n}BuZn [with loss of TMP(H)]; (ii) ^{t}BuZn(TMP) [with loss of ^{n}Bu(H)]; or (iii) ^{n}BuZn(TMP) [with loss of ^{t}Bu(H), *sec*-butane]. ^{1}H NMR spectroscopic studies of the mother liquor shows signals for free TMEDA and both *n*-butyl and *tert*-butyl ligands as well as TMP and TMP(H). This suggests that an alkyl redistribution

process for the zinc compounds akin to the one shown in Scheme 6.

Scheme 6. Redistribution and equilibria which may be involved in the formation of **10**.

Undoubtedly, one of the most important synthetic functions of **1** has been its use as a regioselective base.[37-40] Thermodynamically, it has mainly been demonstrated to function as an alkyl base with ultimate loss of ^{t}Bu-H (*sec*-butane), although synthetic and computational studies have shown that it actually functions in a two-step manner, where an amido group kinetically acts as an amide base (generating an all C_{anion} zincate and amine).[28] This all C_{anion} zincate then re-deprotonates the amine to generate the amido zincate product and alkane. To ascertain whether the alkyl ligands of the hetero-trileptic zincates can be used in synthesis, **5** was reacted with benzene. In contrast to **1**, it was discovered that **5** appeared to be unreactive towards benzene. To put this reaction into context, when **1** is reacted with equimolar quantities of benzene (TMEDA)Na(μ-TMP)(μ-C_6H_5)Zn^{t}Bu is formed in a facile manner.[37] Dideprotonation of benzene using a related mixture, [*i.e.*, *in-situ* preparation of 'Na(TMP)(^{t}Bu)Zn^{t}Bu' in the presence of benzene, followed by TMEDA] produces (TMEDA)Na(μ-TMP)(^{t}Bu)Zn(μ-C_6H_4)Zn(^{t}Bu)(μ-TMP)Na(TMEDA) **11**.[59] Keeping this latter reaction in mind, we altered the reaction to employ the heteroleptic 'Na(TMP)(^{n}Bu)Zn^{t}Bu' zincate, followed by addition of TMEDA. X-ray crystallography and NMR spectroscopic studies showed that **11** appeared to be the only metallated product from this reaction, indicating that thermodynamically 'Na(TMP)(^{n}Bu)Zn^{t}Bu' seems to react as a ^{n}Bu base here. In a major departure from the chemistry associated with **1**, **5** appeared to be unreactive towards toluene,[60] anisole[39] and *N*,*N*-dimethylbenzamide.[35, 61]



Scheme 7. Synthesis of the previously reported dizincated benzene-containing **11**.

Finally, it has been shown recently that **1** can perform single electron transfer (SET) reactions.[43] To ascertain whether **5** is capable of carrying out such reactions, it was reacted with the oxy radical TEMPO (2,2,6,6-tetramethylpiperidinyloxy). This radical has been employed in main group organometallic chemistry[62-64] in recent years and has also been proven to be an important additive in cross-coupling applications.[65-67] When reacted with **1**, it is possible to isolate zincates which contain either one or two TEMPO^{-} anions (*i.e.*, the TEMPO free radical has been reduced to a TEMPO anion), releasing a free alkyl radical. Due to the different nature of the two alkyl groups present in **5**, it could be envisaged that the liberation of the most stable radical (presumably the ^{t}Bu· radical, due to its tertiary nature) would occur. When an equimolecular mixture of ^{n}BuNa, ^{t}Bu$_2$Zn, TMPH, TMEDA and TEMPO is reacted in hexane, a pink solution is obtained immediately but unfortunately no crystalline material was obtained at low temperatures. At this point, the reaction ratio was changes to 2:1 in terms of TEMPO to **5**. After stirring for two hours, then storing at −28°C, X-ray quality crystals of (TMEDA)Na(μ-TMP)(μ-TEMPO)Zn^{n}Bu **12** were produced, showing that **5** has as expected, formally lost its ^{t}Bu ligand producing *s*-butane and isobutene (Scheme 8).

Scheme 8. Synthesis of (TEMPO$^{\cdot}$) zincate (**12**).

Single Crystal X-ray Diffraction Studies

Compound **2** crystallizes in the space group P 2_1/n (Figure 1) as a cocrystal with (PMEDTA)·Na(μ-CH_2SiMe_3)$_2$Zn^{t}Bu. The two complexes share a (disordered) site in the crystal with the site occupancy factor of **2** refining to 84.1(4)%. The disorder means that the accuracy of the model is lower than normal. However, it can be said that the sodium zincate **2** is monomeric, and the Zn atom is surrounded by three alkyl groups [comprised of two *tert*-butyl groups and one (trimethylsilyl)methyl group]. The Zn adopts a distorted trigonal planar environment [range of angles and total, 114.4(3)-124.0(2)°; and 359.7° respectively]. This is in keeping with other sodium zincates where the environment of

the Zn atoms changes from linear in $^{t}Bu_2Zn$ to trigonal planar.[36, 37, 55] The sodium atom has a distorted tetrahedral geometry, and is surrounded by the three nitrogen atoms of the PMDETA [range of N-Na-N angles 76.69(18)-112.4(2)°] and the anionic carbon atom of the (trimethylsilyl)methyl group. For the bridging CH_2 group, the Na-C11 distance is 2.686(6) Å and is similar to those observed in related zincates.[36, 37, 55] There is also a much longer distance interaction between Na1 and a methyl group of the disordered butyl ligand [> 3.00 Å]. This can perhaps be considered as an agostic-type interaction.

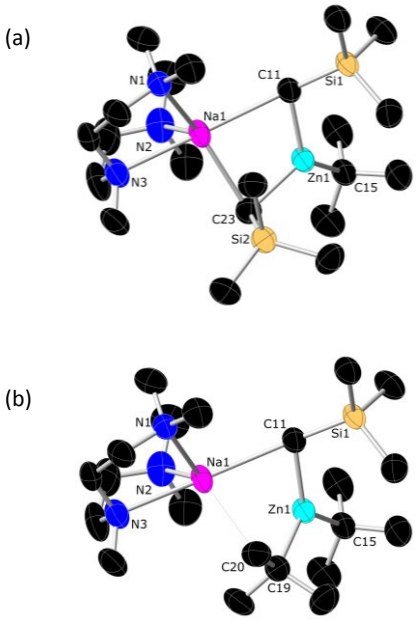


Figure 1. Molecular structure of **2**. Complex **2** is a mix of bridging ^{t}Bu (a) and bridging silyl (b) ligand (approximately 15% silyl). Hydrogen atoms and disorder in ^{t}Bu groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths for **2** (a) [Å] and angles [°]: Na1-N2 2.426(6), Na1-N1 2.437(5), Na1-N3 2.491(6), Na1-C11 2.686(6), Na1-C23 2.56(4), Zn1-C11 2.060(6), Si1-C11 1.836(6), Zn1-C15 2.052(6), N2-Na1-N1-112.4(2), N2-Na1-N3 75.6(2), N1-Na1-N3 75.40(18), N2-Na1-C11 110.5(2), N1-Na1-C11 99.70(18), N3-Na1-C11 173.5(2), Zn1-C11-Na1 76.69(18), C15-Zn1-C19 121.3(3), C15-Zn1-C11 124.0(2), C11-Zn1-C19 114.3(3).

Compound **3** crystallizes in the *P* $2_1/n$ group. (Figure 2). Unlike the conventional bimetallic zincate motif which is prominent (including for **2**), **3** is a tetranuclear disodium dizinc complex whereby the unit cell consists of a Zn atom which is coordinated to three alkyl groups and a Na atom which is coordinated to the three nitrogen atoms of the PMEDTA donor ligand. The alkali metal's coordination sphere within the unit cell is completed by a short Na-CH_2 (Na1-C14) interaction [2.754(3) Å]. This unit cell dimerises via a Na-CH_3 agostic-type interaction [Na1-C10, 2.769(3) Å] that within experimental error is identical to that in **1** [*c.f.*, Na-CH_3 in **1**, 2.750(10) Å]. Hence, these data show that both Na-C bond lengths in **3** are identical within experimental error despite one C atom being anionic (C14) and the other being neutral (C10). Complex **3** can be viewed as a three-element, ten-membered [Na-C-C-Zn-C]$_2$ ring. To the best of our knowledge this type of ring motif for alkali metal zincates is unknown.

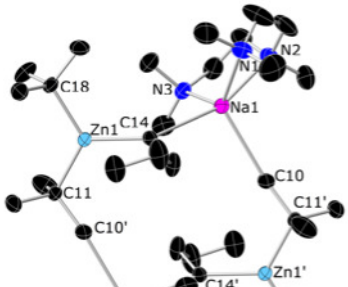


Figure 2. Molecular structure of **3**. Hydrogen atoms and disorder in ^{t}Bu groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths [Å] and angles [°]: Na1-N1 2.471(3), Na1-N2 2.463(3), Na1-N3 2.453(3), Na1-C14 2.754(3), Na1-C10 2.769(3), Zn1-C14 2.060(3), Zn1-C11 2.057(3), Zn1-C18 2.058(3), N3-Na1-N1 122.84(9), N2-Na1-N1 74.43(9), N3-Na1-N2 76.37(9), N3-Na1-C14 91.89(9), N2-Na1-C14 160.98(10), N1-Na1-C14 100.60(9), N3-Na1-C10 107.46(12), N2-Na1-C10 98.53(11), N1-Na1-C10 124.62(11), C14-Na1-C10 99.26(10), C18-Zn1-C14 119.75(11), C11-Zn1-C14 118.63(11), C11-Zn1-C18 121.01(11), Zn1-C14-Na1 144.43(13), C11-C10-Na1 167.2(3).

Compound **4** crystallizes in the *P* $2_1/n$ space group. (Figure 3). Its metal-anion motif is typical of previously reported sodium zincate systems. It reveals the formation of a bis(alkyl) amido complex in which one ^{t}Bu (from **1**) has been replaced by a TMP ligand. Both metal cations adopt distorted trigonal planar motifs (sum of angles around Na1 and Zn, 359.9 and 360.0° respectively). Na1 is bound to a TMP and a *n*-butyl anion, and its coordination sphere is completed by a TMP(H) molecule. Zn1 is bound to three different anions, namely a TMP, *n*-butyl and *t*-butyl. As expected the Na-N_{amide} bond [Na1-N1, 2.3587(15) Å] is significantly shorter that the Na-N_{amine} bond [Na1-N2, 2.4536(16) Å]; and the Zn-$C_{terminal}$ bond [Zn1-C15, 2.0363(18) Å] is slightly shorter than the Zn-$C_{bridging}$ bond [Zn1-C10, 2.0710(17) Å].

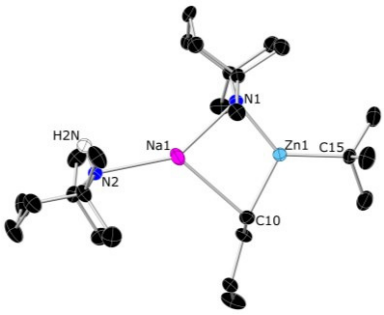


Figure 3. Molecular structure of **4**. Hydrogen atoms are omitted for clarity (30% ellipsoid probability). Selected bond lengths [Å] and angles [°]: Na1-N1 2.3587(15), Na1-N2 2.4536(16), Na1-C10 2.700(2), Zn1-N1 2.0139(14), Zn1-C10 2.0710(17), Zn-C15 2.0363(18), N1-Na1-N2 147.73(6), N1-Na1-C10 84.61(5), N2-Na1-C10 127.59(6), N1-Zn1-C10 113.39(7), N1-Zn1-C15 130.79(6), C10-Zn1-C15 115.82(7).

Compound **5** crystallizes in the orthorhombic system, *Pnma* space group, with a crystallographically imposed mirror plane running through the central Zn-N-Na-C ring (Figure 4). It has the same metal–anion framework as **4**, but in **5** the Na cation is coordinated to the bidentate ligand TMEDA. Complex **5** is the most apt complex to compare with the well-studied and utilised

1, as they are both TMEDA-solvated bis(alkyl)-TMP sodium zincates – the only difference between them is that the former contains three different anions (*tert*-butyl, *n*-butyl and TMP) whilst the latter contains two *tert*-butyl and a TMP anion. In **1**, the Na cation does not formally bond with the anionic C of the 'bridging' *t*-butyl anion. Instead it agostically coordinates to an adjacent CH_3 group. The consequence of this interaction is that a five-membered Na-N-Zn-C-C ring is obtained. In **5**, presumably due to the lower steric demand of ^{n}Bu versus ^{t}Bu the Na cation bonds to the bridging anionic CH_2 of the ^{n}Bu ligand, resulting in a four-membered Na-N-Zn-C ring. The internal angles of this irregular trapezoid range from 80.93(5)° (for the N1-Na1-C4 angle) to 106.66(6)° (for the N1-Zn1-C4 angle), whilst the sum of the angles is 360°. The Na-N_{TMP} distance is 2.3846(13) Å, and as expected is slightly shorter than the Na-N_{TMEDA} bond distance [2.505(10) Å]. To the best of our knowledge, there appears to be only one other example reported of a completely heteroleptic bisalkyl-amido zincate in the literature. Reported by Mulvey and co-workers, in which an alkyl-amido-pyrrolidide complex [(TMEDA)NaZn(TMP)(*α*-C_4H_7*N*Boc)(^{t}Bu)], was obtained by reaction of **1** with a molar equivalent of *N*-Boc pyrrolidine.[68]

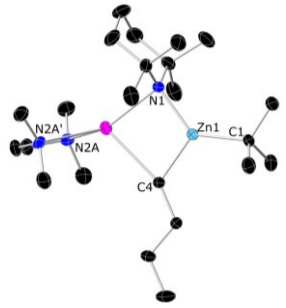


Figure 4. Molecular structure of **5**. Hydrogen atoms and disorder in the TMEDA group are omitted for clarity (30% ellipsoid probability). Selected bond lengths [Å] and angles [°]: Na1-N1 2.3846(13), Na1-N2A 2.505(10), Zn1-N1 2.0340(13), Na1-C4 2.6689(18), Zn1-C1 2.0461(15), Zn1-C4 2.0635(15), N1-Na1-C4 80.93(5), N1-Na1-N2A' 141.3(2), N1-Na1-N2A 135.90(19), N2A'-Na1-C4 106.81(18), N2A-Na1-C4 114.66(18), Zn1-N1-Na1 90.28(5), N1-Zn1-C4 106.66(6), Zn1-C4-Na1 82.12(5).

Complex **6** crystallizes in the triclinic system, *P* -1 space group (Figure 5). In keeping with **5**, **6** is a bimetallic sodium zincate in which a Me_3SiCH_2 ligand has replaced a *tert*-butyl group of **5**. Compound **6** has the same structural motif as described for **5** with the zinc atom adopting a distorted trigonal planar geometry [range of angles around Zn1; and total, 103.91(9)-128.47(9)°; and 359.9° respectably). The Na atom adopts a highly distorted tetrahedral geometry with angles ranging from 76.57(8) Å for the [N2-Na-N3] angle to 140.26(8) Å for the [N1-Na-N3] angle. The Na-C17 length distance [2.721(3) Å], is longer than the respective distance in **4** [2.700(2) Å] and **5** [2.6689(18) Å]. The remaining key bond lengths are in keeping with similar structures. As discussed previously, high quality crystals suitable for X-ray diffraction could not be obtained for *cis*-DMP-containing **7** could not be obtained; however, crystals and data for two other amido-zincates were acquired.

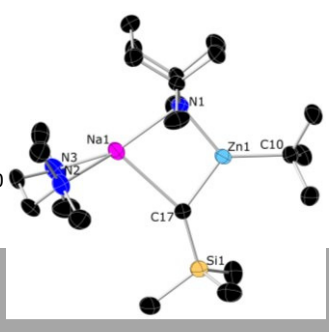


Figure 5. Molecular structure of **6**. Hydrogen atoms and disorder in TMP and TMEDA groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths [Å] and angles [°]: Na1-N1 2.375(2), Na1-N2 2.472(2), Na1-N3 2.464(2), Na1-C17 2.721(3), Zn1-N1 2.041(2), Zn1-C10 2.045(2), Zn1-C17 2.060(3), N1-Na1-N3 140.18(9), N1-Na1-N2 140.26(8), N3-Na1-N2 76.57(8), N1-Na1-C17 78.32(8), N3-Na1-C17 110.55(9), N2-Na1-C17 105.80(9), Zn1-N1-Na1 93.86(8), N1-Zn1-C17 103.91(9), Zn1-C17-Na1 83.91(9), C10-Zn1-C17 127.47(10), N1-Zn1-C10 128.47(9).

Complex **8**, containing the HMDS ligand, crystallizes in the orthorhombic system, *Pnma* space group and again the Zn-N-Na-C ring is coincident upon the crystallographically imposed mirror plane (Figure 6). Unfortunately all the organic groups in **8** are disordered to some extent preventing discussion of the structural parameters. However, As alluded to earlier, **8** has a completely different structure to that found when **1** is reacted with HMDS(H) namely. In this latter reaction the solvent-separated system $[(TMEDA)_2Na]^+[Zn^tBu_2(HMDS)]^-$ is produced.[58] In an attempt to prepare a solvent-separated system akin to this complex, a further equivalent of TMEDA was added; however, only **8** could be isolated.

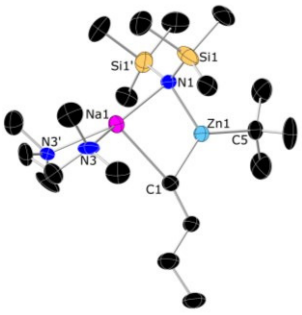


Figure 6. Molecular structure of **8**. Hydrogen atoms and disorder in all organic groups are omitted for clarity (30% ellipsoid probability). Selected bond lengths [Å] and angles [°]: Na1-N1 2.431(3), Na1-C1 2.747(4), Zn1-N1 2.064(3), Zn1-C1 2.028(3), Zn1-C5 2.017(3), Zn1-N1-Na1 89.41(10), C1-Zn1-N1 108.99(12), Zn1-C1-Na1 81.78(11), N1-Na1-C1 79.82(10), C5-Zn1-N1 120.91(13), C5-Zn1-C1 130.09(14), N1-Na1-N2 135.7(3), N1-Na1-N3 143.8(4), N2-Na1-N3 76.5(2), N2-Na1-C1 111.6(3), N3-Na1-C1 105.7(4).

Complex **9** crystallizes in the monoclinic system, *P* 2_1 space group (Figure 7). The asymmetric unit contains two crystallographically independent molecules (Z' = 2). One of these molecules appears to be well ordered, whilst the second has disorder in parts of all of the organic groups. Only geometric parameters for the well-ordered molecule are discussed below. Complex **9** is a monomeric dinuclear sodium zincate. The chiral amide bridges between the two metals, and the Na cation's coordination sphere is completed by bonding to a TMEDA molecule. Rather surprisingly, the Na···CH_2 interaction is considerably longer than in its achiral congeners [2.968(3) Å], so this structure adopts an essentially open motif. As a consequence, the Na-N_{PEA} bond distance [2.344(2) Å] is shorter than the corresponding Na-N_{TMP} distances in **2-6**. The Zn-N bond

do not differ significantly in these complexes and in keeping with the other zincates, the Zn atom is three coordinate and its coordination sphere is completed by bonding to a *tert*-butyl and a *n*-butyl ligand.

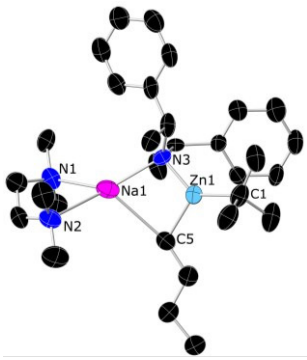


Figure 7. Molecular structure of **9**. Hydrogen atoms are omitted for clarity (30% ellipsoid probability). There are two molecules in the asymmetric unit, only one is shown for clarity. Selected bond lengths [Å] and angles [°]: Na1-N3 2.344(2), Na1-N1 2.432(3), Na1-N2 2.459(2), Na1-C5 2.968(3), Zn1-N3 2.059(2), Zn1-C5 2.038(3), Zn1-C1 2.028(3), N3-Na1-N1 140.85(9), N3-Na1-N2 135.01(8), N1-Na1-N2 76.79(8), N3-Na1-C5 79.01(8), N1-Na1-C5 99.60(9), N2-Na1-C5 127.10(9), C1-Zn1-C5 122.96(11), C1-Zn1-N3 124.17(10), C5-Zn1-N3 112.78(10), Zn1-N3-Na1 86.25(7), Zn1-C5-Na1 71.41(8).

Complex **10** crystallises in the space group and the data reveals dimers which have crystallographically imposed centrosymmetry, and there are two different dimers within the asymmetric unit. The homometallic sodium amido dimer in which each sodium atom is surrounded by four nitrogen atoms in a pseudo tetrahedral geometry (sum of angles about Na1, 660.7°). Selected key bond distances and angles are given in Figure 8. Several sodium amide dimers akin to **10** are known and their key parameters are similar.[69-82]

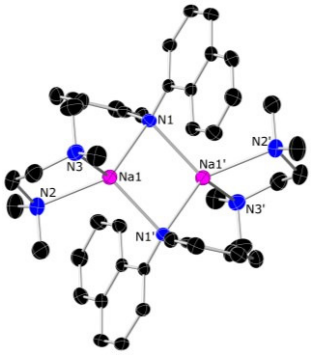


Figure 8. Molecular structure of **10**. Hydrogen atoms and disorder in TMEDA group are omitted for clarity (30% ellipsoid probability). Two independent molecules are present in the asymmetric unit, parameters for one of these are given. Selected bond lengths [Å] and angles [°]: Na1-N1 2.4625(15), Na1-N2 2.4681(17), Na1-N3 2.5499(17), Na1-Na1 3.2807(13), N1-Na1-N2 137.85(6), N2-Na1-N1´ 110.96(5), N1-Na1-N1´ 97.00(5), N1-Na1-N3 113.26(5), N2-Na1-N3 73.85(5), N1´-Na1-N3 127.73(5).

Complex **12** crystallises in the P-1 space group and it has a bimetallic motif which contains a C, N and O anionic ligand set (Figure 9). The sodium atom adopts a distorted tetrahedral N_3O geometry (sum of angles around Na1, 665.1°), whilst the Zn atom is trigonal planar bonding to TMP, ^{n}Bu and TEMPO anions. During the synthesis of **12** from **4** and the TEMPO radical, it is evident the TEMPO has been reduced to an anion and a ^{t}Bu group has been lost (as a radical). The TEMPO N-O bond distance in **12** [1.44(6) Å] is longer than in the free-radical [1.284(8) Å],[83, 84] indicating that reduction has taken place and is comparable to that in that in other main group TEMPO complexes.[62, 63]

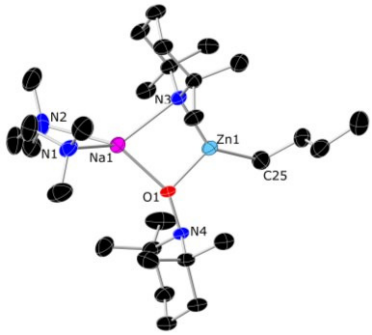


Figure 9. Molecular structure of **12**. Hydrogen atoms and disorder in TMEDA group are omitted for clarity (30% ellipsoid probability). Selected bond lengths [Å] and angles [°]: Na1-O1 2.2546(17), Na1-N1 2.517(16), Na1-N2 2.64(4), Na1-N3 2.462(2), Zn1-O1 1.9477(17), Zn1-N3 1.9874(18), Zn1-C25 1.973(2), O1-N4, 1.446(2), O1-Na1-N1 128.7(2), O1-Na1-N2 134.5(5), O1-Na1-N3 78.52(7), N1-Na1-N2 74.2(5), N1-Na1-N3 128.5(2), N2-Na1-N3 120.7(5), O1-Zn1-N3 78.52(7), O1-Zn1-C25 122.06(9), N3-Zn1-C25 138.39(11).

Finally, when comparing the Zn-$C_{bridging}$, Zn-$C_{terminal}$ and Zn-amide bond distances for **2**-**6**, **8**, **9** and **12**, it is clear that there is only a slight but potentially significant variance in the bond distances between the compounds. Notably when TMP is replaced by a less basic amide (*e.g.*, HMDS or PEA) the Zn-$C_{bridging}$ and Zn-$C_{terminal}$ bonds appear to contract, whereas the Zn-N_{amide} elongate. The all alkyl complexes **2** and **3** can be compared with lithium zincates such as (PMDETA)·Li(μ-Me)$_2$ZnMe.[85] There is an interesting variance in the mean Zn-$C_{bridging}$ and Zn-$C_{terminal}$ bonds in these complexes. For the sodium containing **2** and **3** the mean Zn-$C_{bridging}$ bond distance is 2.059 Å and for (PMDETA)·Li(μ-Me)$_2$ZnMe it is slightly shorter (2.046 Å). The mean Zn-$C_{terminal}$ bond distances in **2** and **3** are 2.055 Å whilst that in the lithium zincate is considerably shorter 2.018(2) Å.

Table 2: Comparison of Zn-C and Zn-N bond distances in **2-6**, **8**, **9** and **12**.

Compound	Zn-$C_{bridging}$ (Å)	Zn-$C_{terminal}$ (Å)	Zn-N_{amide} (Å)
2	2.060(6)	2.052(6)	-
3	2.060(3), 2.058(3)	2.058(3)	-
4	2.0710(17)	2.0363(18)	2.0139(14)
5	2.0635(15)	2.0461(15)	2.0340(13)
6	2.060(3)	2.045(2)	2.041(2)
8	2.028(3)	2.017(3)	2.064(3)
9	2.038(3)	2.028(3)	2.059(2)
12	-	1.973(2)	1.9874(18)

Conclusions

In summary, we have reported the synthesis and characterisation of several novel sodium zincate complexes. It has been demonstrated that amido bia(alkyl) heterotrileptic zincates can be formed, and can undergo a variety of different reactions involving all three of the pendant ligands.

Acknowledgement

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General Methods: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane was dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. ^{n}BuNa was prepared according to the literature procedure.[44] $^{t}Bu_2Zn$ was synthetised according to the literature procedure.[37] TMP(H), *cis*-DMP(H), and PEA(H) were obtained from Sigma-Aldrich and stored over 4 Å molecular sieves prior to use. TMEDA and HMDS(H) were obtained from Sigma-Aldrich and distilled from CaH_2 and stored over molecular sieves. Other chemicals were obtained from Sigma-Aldrich or Alfa Aesar and were used as supplied. NMR spectra were measured on a Bruker AV400 MHz spectrometer. Correlations between proton and carbon atoms were obtained using COSY and HSQC spectroscopic methods.

Crystal structure determinations: Single-crystal data were measured at 123(2) K on Oxford Diffraction Xcalibur and Gemini instruments. The structures were refined to convergence on F^2 and against all independent reflections by full-matrix least squares using the SHELXL-97 program.[86] Due to the highly reactive nature of the zincate species, consistent microanalyses could not be obtained.

Synthesis of [(PMEDTA)·Na(*μ*-CH_2SiMe_3)(*μ*-^{t}Bu)Zn^{t}Bu] (2): (Me_3SiCH_2)Na (0.11 g, 1 mmol) was suspended in hexane (10 mL) and stirred for 5 minutes. A solution of $^{t}Bu_2Zn$ (1 mL of a solution 1 M in hexane, 1 mmol) was added and the resulting clear solution was stirred for 25 minutes. At this stage PMEDTA (0.14 mL, 1 mmol) was added, and the mixture allowed to stir for 1 hour, before being placed into a freezer operating at −28°C to aid crystallisation. A crop of colourless crystals were obtained (0.14 g, 31%). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −1.36 (2H, s, NaCH_2Zn), 0.02 (9H, s, CH_2, $SiMe_3$), 1.02 (18H, s, CH_3, ZnC(CH_3)$_3$), 2.28 (12H, s, N(CH_3)$_2$, PMEDTA), 2.33 (3H, s, NCH_3, PMEDTA), 2.37-2.40 (4H, m, CH_2, PMEDTA), 2.46-2.47 (4H, m, CH_2, PMEDTA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): −3.1 (*C*H_2, *C*H_2Zn), 3.3 (*C*H_2, *C*$H_2$$SiMe_3$), 33.5 (*C*$H_3$, ZnC(*C*$H_3$)$_3$), 33.7 (Zn*C*$CH_3$), 43.4 (N*C*$H_3$, PMEDTA), 45.4 (N(*C*$H_3$)$_2$, PMEDTA), 54.9 (N*C*$H_2$, PMEDTA), 57.1 (N*C*$H_2$, PMEDTA).

Synthesis of [(PMEDTA)·Na(*μ*-^{n}Bu)(*μ*-^{t}Bu)Zn^{t}Bu]$_2$ (3): ^{n}BuNa (0.08 g, 1 mmol) was suspended in hexane (10 mL) and stirred for 5 minutes. A solution of $^{t}Bu_2Zn$ (1 mL of a solution 1 M in hexane, 1 mmol) was added and the resulting clear solution was stirred for 25 minutes. At this stage PMEDTA (0.14 mL, 1 mmol) was added, and stirred for one hour. The solution and then placed into the freezer operating at −28 °C to aid crystallisation. Suitable crystals for X-ray diffraction analysis were obtained; however the crystals redissolved at ambient temperature during filtration. NMR analysis of the solution was performed. ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −0.13 (2H, t, $^3J_{HH}$ = 10.0 Hz, NaCH_2Zn), 0.92 (3H, t, $^3J_{HH}$ = 7.2 Hz, CH_3, Bu), 1.05 (18H, s, CH_3, ZnC(CH_3)$_3$), 1.30-1.36 (2H, m, CH_2, Bu), 1.60-1.67 (2H, m, CH_2, Bu), 2.27 (12H, s, N(CH_3)$_2$, PMEDTA), 2.32 (3H, s, NCH_3, PMEDTA), 2.40-2.42 (4H, m, CH_2, PMEDTA), 2.48-2.94 (4H, m, CH_2, PMEDTA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 12.1, (*C*H_2, ^{n}Bu), 13.6 (*C*H_3, ^{n}Bu), 30.5 (*C*H_2, ^{n}Bu), 32.4 (*C*H_2, ^{n}Bu), 33.6 (*C*H_3, ZnC(*C*H_3)$_3$), 35.3 (Zn*C*CH_3), 42.7 (N*C*H_3, PMEDTA), 45.4 (N(*C*H_3)$_2$, PMEDTA), 55.8 (N*C*H_2, PMEDTA), 57.3 (N*C*H_2,PMEDTA).

Synthesis of [(TMPH)·Na(*μ*-TMP)(*μ*-^{n}Bu)Zn^{t}Bu] (4): ^{n}BuNa (0.32 g, 4 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of $^{t}Bu_2Zn$ (4 mL of a solution 1 M in hexane, 4 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.68 mL, 4 mmol) was then introduced and the mixture was stirred at ambient temperature for 10 minutes until all the solid had dissolved. The solution was heated slightly before placed in the freezer at −28 °C, the resulting pale yellow solution deposited a crop of white crystals (0.65 g, 66%; based on TMPH consumption). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −0.35 - −0.29 (2H, m, CH_2, Bu), 0.91 (3H, t, $^3J_{HH}$ = 7.2 Hz, Bu), 1.06 (9H, s, CH_3, ZnCCH_3), 1.07-1.20 (12H, s, TMPH), 1.21 (12H, s, TMP), 1.30-1.36 (2H, m, CH_2, Bu), 1.39-1.42 (6H, m, CH_2, Bu and TMP), 1.58-1.74 (8H, m, CH_2, Bu and TMP). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 13.5 (*C*H_3, Bu), 16.6 (Zn*C*H_2, Bu), 17.7 (*C*H_2, TMP), 19.5 (*C*H_2, TMP), 20.2 (Zn*C*(CH_3)$_3$), 30.2 (ZnC(*C*H_3)$_3$), 31.0 (*C*H_2, Bu), 31.5 (*C*H_3, TMP), 32.2 (*C*H_2, Bu), 34.1 (*C*H_3, TMP), 38.2 (CH_2, TMP), 40.0 (CH_2, TMP), 50.5 (N−*C*, TMP), 52.3 (N−*C*, TMP).

Synthesis of [(TMEDA)Na(*μ*-TMP)(*μ*-^{n}Bu)Zn^{t}Bu] (5): ^{n}BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of $^{t}Bu_2Zn$ (2 mL of a solution 1 M in hexane, 2 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.34 mL, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.30 mL, 2 mmol) was added, stirring for 15 minutes and the solution is heated slightly before placed in the freezer at −28 °C, the resulting pale yellow solution deposited a crop of white crystals (0.55 g, 60%). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −0.43 - −0.39 (2H, m, CH_2, Bu), 0.91 (3H, t, $^3J_{HH}$ = 6.0 Hz, Bu), 1.05 (12H, s, TMP), 1.14 (9H, s, CH_3, ZnCCH_3), 1.28-1.33 (2H, m, CH_2, Bu), 1.56-1.61 (2H, m, CH_2, Bu), 2.31 (12H, s, N(CH_3)$_2$, TMEDA), 2.41 (4H, s, NCH_2, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 13.6 (*C*H_3, Bu), 16.6 (Zn*C*H_2, Bu), 19.6 (*C*H_2, TMP), 20.1 (Zn*C*(CH_3)$_3$), 31.3 (*C*H_2, Bu), 32.6 (*C*H_2, Bu), 34.0 (ZnC(*C*H_3)$_3$), 34.4 (*C*H_3, TMP), 39.7 (CH_2, TMP), 45.8 (N(*C*H_3), TMEDA), 52.1 (N−*C*, TMP), 57.2 (N*C*H, TMEDA).

Synthesis of [(TMEDA)·Na(*μ*-TMP)(*μ*-CH_2SiMe_3)Zn^{t}Bu] (6): (Me_3SiCH_2)Na (0.22 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of $^{t}Bu_2Zn$ (2 mL of a solution 1 M in hexane, 2 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.34 mL, 2 mmol) was then introduced and the mixture was stirred at ambient temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.30 mL, 2 mmol) was added, stirring for 15 minutes and the solution was then gently heated before being placed in the freezer operating at −28 °C, the resulting

pale yellow solution deposited a crop of colourless crystals (0.59 g, 61%). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −1.42 (2H, s, CH_2, Bu), 0.02 (9H, s, Si(CH_3)$_3$), 1.03-1.17 (23H, m, ZnC(CH_3)$_3$, and TMP), 1.55-1.74 (4H, m, CH_2, TMP), 2.31 (12H, s, N(CH_3)$_2$, TMEDA), 2.41 (4H, s, NCH_2, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): −0.8 (*C*H$_2$, Zn*C*H$_2$), 3.5 (*C*H$_3$, SiMe$_3$), 19.0 (Zn*C*(CH$_3$)$_3$), 19.5 (*C*H$_2$, TMP), 34.5 (*C*H$_3$, TMP), 35.4 (ZnC(*C*H$_3$)$_3$), 39.4 (*C*H$_2$, TMP), 46.1 (N(*C*H3), TMEDA), 52.4 (N−*C*, TMP), 57.4 (N*C*H, TMEDA).

Synthesis of [(TMEDA)·Na(*μ*-*cis*-DMP)(*μ*-^{n}Bu)Zn^{t}Bu] (7): ^{n}BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of ^{t}Bu$_2$Zn (2 mL of a solution 1 M in hexane, 2 mmol) was added and the resulting clear solution was stirred for 5 minutes. *cis*-DMP(H) (0.28 mL, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.30 mL, 2 mmol) was added, stirring for 15 minutes and the solution was gently heated before being placed into a freezer operating at −28 °C, the resulting pale yellow solution deposited a crop of white crystals (0.38 g, 42%). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −0.40 (2H, t, $^3J_{HH}$ = 8.0 Hz, CH_2, Bu), 0.36-0.39 (2H, m, CH_2, *cis*-DMP), 0.88-0.92 (3H, t, $^3J_{HH}$ = 16.0 Hz, CH_3, Bu), 0.95-0.97 (6H, m, CH_3, *cis*-DMP), 1.01 (9H, s, ZnC(CH_3)$_3$), 1.27-1.33 (2H, m, CH_2, Bu), 1.62-1.76 (6H, m, CH_2, *cis*-DMP and Bu), 2.31 (12H, s, N(CH_3)$_2$, TMEDA), 2.41 (4H, s, NCH_2, TMEDA), 3.03-3.07 (2H, m, CH_2, *cis*-DMP). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 13.6 (*C*H$_3$, Bu), 15.9 (Zn*C*H$_2$, Bu), 25.5 (Zn*C*(CH$_3$)$_3$), 26.0 (*C*H$_3$, *cis*-DMP), 30.7 (*C*H$_2$, Bu), 32.3 (*C*H$_2$, Bu), 34.1 (ZnC(*C*H$_3$)$_3$), 39.1 (CH$_2$, *cis*-DMP), 45.6 (N(*C*H$_3$), TMEDA), 55.7 (*C*H, *cis*-DMP), 56.6 (N*C*H, TMEDA), 57.1 (CH$_2$, DMP).

Synthesis of [(TMEDA)·Na(*μ*-HMDS)(*μ*-^{n}Bu)Zn^{t}Bu] (8): ^{n}BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of ^{t}Bu$_2$Zn (2 mL of a solution 1 M in hexane, 2 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.34 mL, 2 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.30 mL, 2 mmol) was added, stirring for 15 minutes. One molar equivalent of the amine HMDS(H) (0.42 mL, 2 mmol) was then introduced. On addition of this amine an orange solution was obtained which was allowed to stir at ambient temperature for one hour before being placed into a freezer operating at −28 °C to aid crystallisation. A crop of colourless crystals was obtained (0.43 g, 45%). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): -0.33 (2H, t, $^3J_{HH}$ = 8.0 Hz, CH_2, Bu), 0.07 (18H, s, CH_3, Si(CH_3)$_3$), 0.92 (3H, t, $^3J_{HH}$ = 7.2 Hz, CH_3, Bu), 1.05 (9H, s, ZnCCH_3), 1.29-1.35 (2H, m, CH_2, Bu), 1.65-1.69 (2H, m, CH_2, Bu), 2.32 (12H, s, N(CH_3)$_2$, TMEDA), 2.41 (4H, s, NCH_2, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 5.0 (*C*H$_3$, SiC(*C*H$_3$)$_3$), 13.5 (*C*H$_3$, ^{n}Bu), 16.3 (Zn*C*H$_2$, ^{n}Bu), 21.4 (Zn*C*(CH$_3$)$_3$), 30.8 (*C*H$_2$, ^{n}Bu), 32.2 (*C*H$_2$, ^{n}Bu), 33.4 (ZnC(*C*H$_3$)$_3$), 46.0 (N(CH$_3$), TMEDA), 57.1 (N*C*H, TMEDA).

Synthesis of [(TMEDA)·Na(*μ*-PEA)(*μ*-^{n}Bu)Zn^{t}Bu] (9): ^{n}BuNa (0.16 g, 2 mmol) was suspended in hexane (15 mL) and stirred for 5 minutes. A solution of ^{t}Bu$_2$Zn (2 mL of a solution 1 M in hexane, 2 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.34 mL, 2 mmol) was then introduced and the mixture was stirred at ambient temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.30 mL, 2 mmol) was added, before stirring the mixture for 15 minutes. One molar equivalent of the chiral amine (*R*)-*N*- bis[(*R*)-α-methylbenzyl]amine (0.44 mL, 2 mmol) was then introduced. On addition of this amine an orange solution was obtained which was allowed to stir at ambient temperature for one hour and the solution and then placed into the freezer at −28 °C to aid crystallization. A crop of white crystals were obtained (0.53 g, 48%). ^{1}H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): −0.48 - −0.28 (2H, m, CH_2Si(CH$_3$)$_3$), 0.92 (12H, t, $^3J_{HH}$ = 7.2 Hz, CH_3, Bu and ZnC(CH_3)$_3$), 1.26 (6H, d, $^3J_{HH}$ = 6.4 Hz, CH_3, PEA), 1.28-1.33 (2H, m, CH_2, Bu), 1.63-1.69 (2H, m, CH_2, Bu), 2.25 (12H, s, N(CH_3)$_2$, TMEDA), 2.38 (4H, s, NCH_2, TMEDA), 3.96 (2H, br, NC*H*CH$_3$, PEA), 7.05-7.21 (10H, m, Ph, PEA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 13.5 (*C*H$_3$, ^{n}Bu), 16.8 (*C*H$_2$, ^{n}Bu), 22.6 (Zn*C*CH$_3$), 26.1 (*C*H$_3$, PEA), 31.0 (*C*H$_2$, ^{n}Bu), 32.5 (*C*H$_2$, ^{n}Bu), 33.2 (*C*H$_3$, ZnC(*C*H$_3$)$_3$), 45.6 (N(*C*H$_3$), TMEDA), 57.2 (N*C*H, TMEDA), 60.4 (N*C*HCH$_3$, PEA), 125.4, 126.1, 127.8 (*C*H, Ar), 146.0 (C_{ipso}, Ar).

Synthesis of [(TMEDA)·Na(*μ*-NPhNPh)]$_2$ (10): ^{n}BuNa (0.08 g, 1 mmol) was suspended in hexane (10 mL) and stirred for 5 minutes. A solution of ^{t}Bu$_2$Zn (1 mL of a solution 1 M in hexane, 1 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.17 mL, 1 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 1 mmol) was added, before stirring the mixture for 15 minutes. One molar equivalent of the amine *N*-phenylnaphthalen-2-amine (0.22 g, 1 mmol) was then introduced. On addition of this amine a yellow solid was obtained. The solid was filtrated via cannula and stored in a glove box. (0.24 g, 66%). Suitable crystals for X-ray diffraction were obtained by cooling a hot THF-hexane solution of this compound slowly. ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): 1.54 (16H, bs, CH_3 and CH$_2$, TMEDA), 6.62-6.66 (1H, m, Ar), 7.00-7.05 (m, 3H, Ar), 7.17-7.19 (m, 2H, Ar), 7.25-7.30 (3H, m, Ar), 7.39-7.43 (1H, m, Ar), 7.77-7.79 (1H, d, $^3J_{HH}$ = 8 Hz, Ar), 8.31-8.33 (1H, m, Ar). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): 13.5, (*C*H$_3$, ^{n}Bu), 16.8 (*C*H$_2$, ^{n}Bu), 22.6 (Zn*C*CH$_3$), 26.1 (*C*H$_3$, PEA), 31.0 (*C*H$_2$, ^{n}Bu), 32.5 (*C*H$_2$, ^{n}Bu), 33.2 (*C*H$_3$, ZnC(*C*H$_3$)$_3$), 45.6 (N(*C*H$_3$), TMEDA), 57.2 (N*C*H, TMEDA), 60.4 (N*C*HCH$_3$, PEA), 125.4, 126.1, 127.8 (*C*H, Ar), 146.0 (C_{ipso}, Ar).

Synthesis of [(TMEDA)·Na(*μ*-TMP)(*μ*-TEMPO)Zn^{n}Bu] (12): ^{n}BuNa (0.08 g, 1 mmol) was suspended in hexane (5 mL) and stirred for 5 minutes. A solution of ^{t}Bu$_2$Zn (1 mL of a solution 1 M in hexane, 1 mmol) was added and the resulting clear solution was stirred for 5 minutes. TMP(H) (0.17 mL, 1 mmol) was then introduced and the mixture was stirred at room temperature for 10 minutes until all the solid had dissolved. At this stage TMEDA (0.15 mL, 1 mmol) was added, stirring for 15 minutes. Two molar equivalents of TEMPO (0.31 g, 2 mmol) were then introduced. On addition of this radical, a pink-yellow solution was obtained which was allowed to stir at ambient temperature for one hour. The solution was then placed into a freezer operating at −28 °C to aid crystallization. A crop of white crystals were obtained (0.12 g, 22%). ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): 1.27-1.70 (46H, m, overlap signals for ^{n}Bu, TMP and TEMPO), 1.84-1.87 (2H, m, CH_2, Bu), 2.00-2.05 (16H, m, N(CH_3)$_2$ and NCH_2, TMEDA). ^{13}C{^{1}H} NMR (100.62 MHz, 298 K, C_6D_6): 12.6 (*C*H$_2$, ^{n}Bu), 13.0 (*C*H$_2$, ^{n}Bu), 14.2 (*C*H$_3$, ^{n}Bu), 14.6 (*C*H$_3$, ^{n}Bu), 17.9 (*C*H$_2$), 18.7 (*C*H$_2$), 20.2 (Zn*C*CH$_3$), 20.5 (*C*H$_3$), 29.5 (*C*H$_3$), 29.9 (*C*H$_2$), 31.2 (*C*H$_2$), 32.0 (*C*H$_3$), 34.2, 34.5, 35.0, 35.4 (4 x *C*H$_3$), 39.2 (*C*H$_2$), 41.0 (*C*H$_2$), 46.2 (N(*C*H$_3$), TMEDA), 52.5 (N−*C*), 53.7 (N−*C*), 57.8 (N*C*H, TMEDA).

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