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ARTICLE

New Supramolecular Assemblies in Heterobimetallic Chemistry: Synthesis of a Homologous Series of Unsolvated Alkali-metal Zincates

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Using an interlocking co-complexation approach, a homologous series of unsolvated alkali-metal zincates [MZn(CH$_2$SiMe$_3$)$_3$] (M = Li **1**, Na **2**, K **3**) was prepared by reacting equimolar amounts of Zn(CH$_2$SiMe$_3$)$_2$ with the relevant alkali-metal alkyl M(CH$_2$SiMe$_3$) employing non-coordinating hexane as a solvent. X-ray crystallographic studies reveal that these heterobimetallic compounds exhibit unprecedented supramolecular assemblies made up exclusively of a three-fold combination of M-CH$_2$, Zn-CH$_2$ and M···Me interactions. Revealing an important alkali-metal effect, **1** displays a linear chain structure; whereas **2** and **3** form much more intricate 3D and 2D coordination networks respectively. Shedding new light into the formation of these solvent-free zincates, DFT calculations indicate that the infinite degree of aggregation observed in **1-3** plays a major role in thermodynamically driving the co-complexation reactions of their homometallic precursors. NMR spectroscopic studies suggest that in C$_6$D$_6$ solution **1-3** exist as discrete contacted ion-pair species, where the alkali-metal is partially solvated by molecules of deuterated solvent. The supramolecular assemblies of **1-3** can be easily deaggregated by adding the polydentate N-donors PMDETA (*N,N,N',N'',N''*-pentamethyldiethylenetriamine) or TMEDA (*N,N,N',N'*-tetramethylethylenediamine), affording monomeric [(PMDETA)LiZn(CH$_2$SiMe$_3$)$_3$] (**4**) and [(TMEDA)$_2$NaZn(CH$_2$SiMe$_3$)$_3$] (**5**).

Introduction

The pool of available synthetically useful polar organometallic reagents has enlarged remarkably in recent years with the development of heterobimetallic reagents combining an alkali-metal with a lower polarity metal, such as Mg, Zn or Al.[1] Many of these new reagents come in the category of ates, such as magnesiates, zincates or aluminates. By switching on cooperative effects, these two-fold metal compounds can exhibit special reactivity patterns, above and beyond what is possible with traditional single-metal reagents. Dating back to 1858, when Wanklyn reported the synthesis of NaZnEt$_3$ by reacting ZnEt$_2$ with sodium metal,[2] alkali-metal zincates represent one of the oldest types of 'ate compounds known in the history of heterobimetallic chemistry.[3] Wankyln's pioneering work already gave some glimpses of the enhanced reactivity of these bimetallic systems when compared with their homometallic counterparts, by describing their reaction with CO$_2$ to afford the relevant carboxylic acids, whereas ZnEt$_2$ on its own is inert towards this electrophilic gas.[4] Nowadays, alkali-metal zincates are well established as reagents in modern organometallic synthesis, finding extensive applications in a

myriad of fundamental organic transformations such as zinc-halogen exchange,[5] epoxide ring openings,[5a,b] nucleophilic additions[6] and deprotonative metallation[7] to name but a few.[1,8]
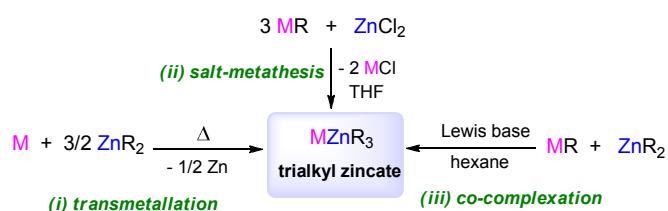
Scheme 1. Main synthetic strategies to prepare homoleptic alkyl alkali-metal zincates

Despite their synthetic usefulness, few alkali-metal zincates, in particular homoleptic alkyl species have been structurally defined.[9] Thus, although Wanklyn's original methodology has proved to be successful for preparing certain triorganozincates (Scheme 1, *i*),[9a] the structure of his cornerstone MZnEt$_3$ (M= Na, K) compounds still remain to be unveiled. Requiring the use of harsh reaction conditions, this approach can be limited

by the thermal stability of the alkyl substituents employed, yielding in some cases mixed alkyl-hydrido species.[10]

Alternatively one can access alkyl zincates via salt-metathesis, by reacting reacting $ZnCl_2$ with an excess of an organo-alkali-metal reagent (Scheme 1, *ii*).[11] However since the use of donor ethereal solvents is required to solubilize the zinc halide, this method precludes the isolation of solvent-free species. Co-complexation reactions of the two homometallic alkyl reagents (Scheme 1, *iii*) has emerged as a third versatile approach which advantageously is compatible with the use of non-coordinating or weakly coordinating solvents.[12] Usually, the addition of a Lewis base (commonly THF or TMEDA) is needed to facilitate the self-assembly of the mixed organometallic reagent, by generating in solution smaller (and more reactive) aggregates of the alkali-metal alkyl precursors that can join up together. By modulating the hapticity of the Lewis base employed and the steric bulk of the alkyl substitutents, different structural motifs have been described, as nicely illustrated by Stalke in a recent study assessing the co-complexation of MeLi and $ZnMe_2$ in the presence of several donor bases.[9d]

Previous efforts to access solvent-free triorganozincates using a weakly coordinating solvent such as benzene have led to the isolation of unexpected heteroleptic species containing Ph substituents, as a result of the metallation of benzene.[9a] For example Lennarston has recently reported the structure of dialkylzincate $[NaZnEt_2Ph]$ while attempting the crystallization of trialkylzincate $[NaZnEt_3]$ from benzene.[13] Furthermore, even in cases where the arene has not been deprotonated but remains fully intact, it can still be incorporated into the local coordination environment of the zincate by engaging the alkali-metal component in π-electrostatic interactions.[14]

Recent work in our group, exploring the synthesis of solvent-free alkyl magnesiates[15] and gallates[16] has led to the isolation of novel heterobimetallic species which exhibit unique supramolecular assemblies. A key feature of these studies is the use of the monosilyl CH_2SiMe_3 group as an anionic ligand. Lacking of β-hydrogens, and therefore resistant to β-hydride decomposition pathways, this ligand can greatly improve the stability of the organometallic species through its bulkiness and electronic stabilization.[17]

Building on this previous related ate work, herein we extend our investigations to the synthesis of a new homologous series of homoleptic alkali-metal zincates $[MZn(CH_2SiMe_3)_3]$ (M = Li **1**, Na **2**, K **3**) by systematically studying the interlocking co-complexation reactions of $Zn(CH_2SiMe_3)_2$ with the alkali-metal alkyl compounds MCH_2SiMe_3 (M = Li, Na, K) in hexane. The influence that the alkali-metal imposes on the structures of these bimetallic species has been quantified by combining X-ray crystallography with NMR spectroscopic studies. In the solid state, these donor-free zincate species exhibit intricate polymeric structures. To shed some light on the energetics involved in the formation of these compounds, DFT calculations on these co-complexation reactions have been carried out, revealing that the infinite level of aggregation in zincates **1-3** plays a major role in these processes. The monomeric structures of $[(PMDETA)LiZn(CH_2SiMe_3)_3]$ (**4**) and $[(TMEDA)_2NaZn(CH_2SiMe_3)_3]$ (**5**) are also presented, obtained by the addition of the relevant polydentate N-donors to the unsolvated zincates $[MZn(CH_2SiMe_3)_3]$ with M= Li and Na respectively.

Results and discussion

Synthesis We began our studies investigating the co-complexation of $LiCH_2SiMe_3$[18] with equimolar amounts of

$Zn(CH_2SiMe_3)_2$[19] using the non-coordinating solvent hexane. This resulted in the immediate formation of a white solid, suggesting the formation of a new compound since both parent components are highly soluble in hexane. This new solid could be redissolved in neat benzene, affording a solution which deposited colourless crystals of homoleptic $[LiZn(CH_2SiMe_3)_3]$ (**1**) (Scheme 1). Compound **1** can be isolated as a pure white solid in an 84% yield when it is prepared using hexane as a solvent.
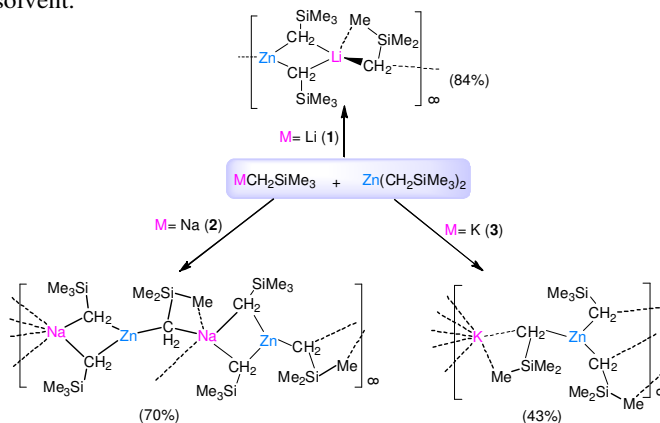
Scheme 2. Co-complexation reactions of $Zn(CH_2SiMe_3)_2$ with MCH_2SiMe_3 (M = Li, Na, K) in hexane to form zincates **1**, **2** and **3** respectively.

The same approach was employed to prepare the sodium and potassium congeners of **1**, $[MZn(CH_2SiMe_3)_3]$ (M= Na,[15] **2**; K,[20] **3**) in a 70 and 43% yield respectively (Scheme 1). In this case the heavier alkali-metal precursors are also scarcely soluble in hexane, however, the formation of **2** and **3** must take place in this solvent, as when hexane is removed under vacuum, and benzene is introduced, no metallation is observed (in contrast both Na and K alkyl species can deprotonate benzene at room temperature).[21] Slow evaporation of these benzene solutions allowed the isolation of **2** and **3** as colourless crystalline solids. It should be noted that the synthesis of **3** has been previously reported by Purdy using Wanklyn's original preparation, by refluxing $Zn(CH_2SiMe_3)_2$ with potassium metal, though under these harsher reaction conditions compound **3** was obtained along with heteroleptic $[KZn(CH_2SiMe_3)_2Ph]$.[9a]
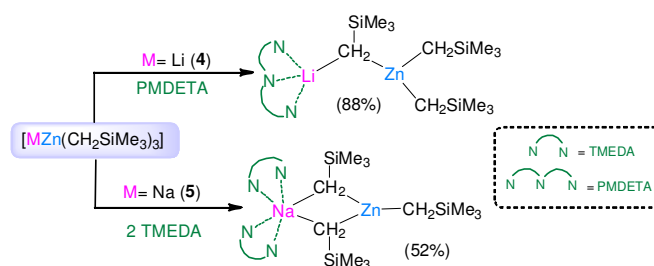
Scheme 3. Deaggregation reactions of **1** and **2** by addition of Lewis donors PMDETA and TMEDA to give zincates **4** and **5** respectively.

Addition of one equivalent of trifunctional amine PMDETA to a suspension of **1** in hexane afforded a colourless solution which on cooling deposited crystals of $[(PMDETA)LiZn(CH_2SiMe_3)_3]$ (**4**) in a 88% yield. A similar observation was noted when two equivalents of bidentate N-

donor TMEDA were introduced to a suspension of **2** in hexane which allowed the isolation of the sodium zincate [(TMEDA)$_2$NaZn(CH$_2$SiMe$_3$)$_3$] (**5**).

Homoalkyl alkali-metal zincates **1-5** were characterized by multinuclear NMR and their structures in the solid state have been elucidated by X-ray crystallographic studies (see Experimental Section and Supporting Information for full details).

Solid-State structures

Crystals of unsolvated zincates **1-3** for analysis by X-ray crystallography were grown by slow evaporation at room temperature of saturated benzene solutions. Contrasting with other alkali-metal zincates crystallized using a similar method,[9a,14b,22] compounds **1-3** do not incorporate solvent molecules coordinating to the alkali-metal.

These studies reveal that all three compounds **1-3** display novel infinitely aggregated structures,[23] made up of a combination of [Zn(CH$_2$SiMe$_3$)$_3$]$^-$ anions and M$^+$ (M = Li, Na, K) cations (see Figures 1, 2, and 3). Despite their identical formulation, each zincate in this homologous series forms a distinct supramolecular assembly; with **1** exhibiting a 1D chain arrangement (Figure 1b);[24] whereas **2** and **3** give rise to more intricate 3D and 2D networks respectively (Figures 2d, 2e and 3b). Each zincate anion in compounds **1** and **2** coordinates to the alkali-metal through the methylene head of two monosilyl groups forming a slightly puckered four-membered {MCZnC} ring (Figures 1 and 2).[25]. The remaining alkyl group on zinc binds to a neighbouring cation in an unsual ambidentate fashion through its CH$_2$ [Li-CH$_2$ 2.241(4); Na-CH$_2$ 2.684(2), 2.697(2) Å] and one methyl of the SiMe$_3$ group [Li···Me 2.515(4); Na···Me 2.816(3), 2.975(3) Å] (Table 1 and Supporting Information), closing a four membered {MCSiC} ring.[25] This connectivity pattern, alternating these two different types of four-membered rings, is extended across the crystallographic *b*-axis for species **1** and **2** leading to the formation of a 1D chain (Figure 1b and 2b). Compound **1** exhibits an infinite near-linear arrangement [Zn···Li···Zn 165.07(12)° and Li···Zn···Li 165.07(9)°] of these {MCZnC} and {MCSiC} rings which are fused by their Li vertexes, in a staggered near orthogonal disposition (angle between planes 88.3; average C-Li-C angle, 108.9°). Contrastingly in sodium zincate **2** the disposition of the metals deviates considerably from linearity [Zn···Na···Zn 172.98(2)°, 163.98(2)° Na···Zn···Na 114.39(2)°, 137.16(2)°], giving rise to a helical chain with the Na atoms adopting a pseudo-square planar geometry (average C-Na-C angle 89.0°). These structural differences can be attributed to the larger size of sodium when compared to lithium. Indeed, comparison of the space filling models of these structures shows that the lithium centers in **1**, with a coordination number four, are completely shielded, the whereas the sodium atoms with the same coordination number in **2** are coordinatively unsaturated within the 1D chain (Figures 1c and 2c). In order to attain a

higher coordination number sodium atoms form additional medium-long electrostatic interactions with other methyl groups belonging either to neighboring zincate units within the same chain or to neighboring chains [Na···Me 2.984 (3), 3.215(2), 3.216(3) Å] (Table 1), which leads to the formation of an eyecatching 3D network where which contains a combination of hexa- and penta-coordinated sodium atoms (Na1 and Na2 respectively) (Figure 2e).

Table 1. Selected bond distances (Å) for alkali-metal zincates **1–5**.

M-CH$_2$	**1**	**2**[a]	**3**	**4**	**5**
M1-C1	2.257(4)	2.700(2)	3.119(3)		3.022(3)
M1-C5[b]	2.226(4)	2.684(2)	3.141(3)	2.388(4)	
M1-C9	2.241(4)	2.670(2)	3.093(3)		3.029(3)
Na2-C5		2.697(2)			
Na2-C17		2.655(2)			
Na2-C21		2.658(2)			
Zn-C1	2.056(2)	2.051(2)	2.044(3)	2.041(2)	2.053(3)
Zn-C5	2.051(2)	2.056(2)	2.042(4)	2.061(2)	2.035(3)
Zn-C9	2.021(2)	2.074(2)	2.057(3)	2.049(2)	2.055(3)
Zn2–C17		2.065(2)			
Zn2–C21		2.052(2)			
Zn2–C13		2.047(2)			

M-CH$_3$					
	1		**2**[a]		**3**
Li-C11	2.515(4)	Na1-C11'	3.215(2)	K1-C3	3.331(4)
		Na1-C14'	2.975(3)	K1-C11'	3.209(5)
		Na1-C20'	2.984(3)	K1-C12'	3.530(4)
		Na2-C7	2.816(3)	K1-C2'	3.417(5)
		Na2-C4'	3.216(3)		

[a]The asymmetric unit of **2** contains two independent NaZn(CH$_2$SiMe$_3$)$_3$ fragments. [b] For compound **2** this distance represents Na1-C13'.

A remarkable alkali-metal effect is also evident for the potassium zincate **3** (Figure 3). Its basic repeat unit comprises a trigonal planar zinc bonded to three monosilyl groups (Figure 3a). Both metals are connected in the asymmetric unit by a single alkyl group which coordinates to K in an η^2-fasion through its CH$_2$ unit [K1-C1, 3.119 (3) Å] and one Me from the SiMe$_3$ group [K1-C3, 3.331(4) Å]. One of the remaining alkyls binds in a similar ambidentate mode to another K atom along the crystallographic *b*-axis [K1-C9, 3.093(3); K1-C11, 3.209(5) Å] whereas the other monosilyl group interacts through its methylene head with a third potassium atom located in a perpendicular disposition, giving rise to an intricate 2D supramolecular assembly. Similarly to sodium in compound **2**, potassium expands its coordination sphere to seven by forming two additional K···Me contacts with neighboring methyl groups [K···Me 3.417(5), 3.530(4) Å] (Figure 3b). These values are similar to those previously reported by Weiss for the structure of [MeK] where K also forms long distance interactions with the Me groups of other units (mean K…Me, 3.441 Å) which are significantly elongated when compared to the K-Me distances towards the carbanion (2.447 Å).[26]
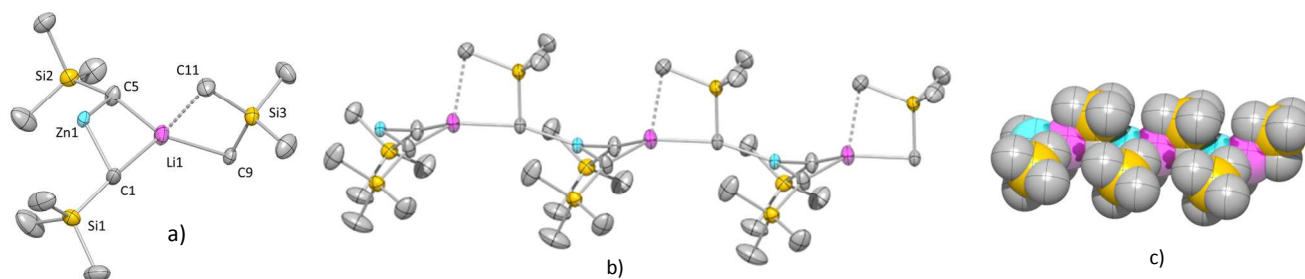
Figure 1. Solid state structure of **1** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Dotted lines represent longer Li-C interactions; a) asymmetric unit; b) 1D polymeric chain; c) space filling model for a section of the polymeric structure.
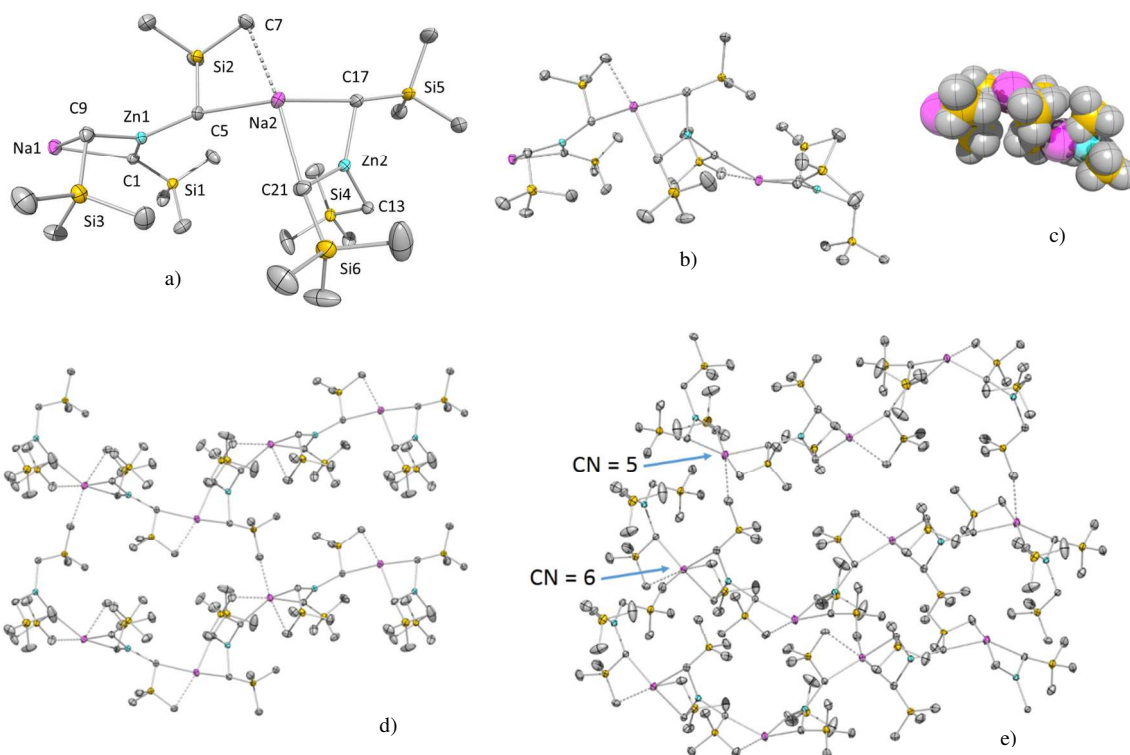

Figure 2. Solid state structure of **2** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity. Dotted lines represent longer Na-C interactions; a) asymmetric unit; b) fragment of the polymeric structure along the crystallographic b-axis; c) space filling model for a section of polymeric structure; d) view of the polymeric structure along the *ab*-plane; e) view of the polymeric structure along the *bc*-plane.

It should be noted that polymorph of **3** has been previously reported by Purdy, prepared as previously mentioned by reaction of elemental potassium with $Zn(CH_2SiMe_3)_3$. Although K is also hepta-coordinated in this structure, it displays well-defined $\{KZn(CH_2SiMe_3)\}_2$ dimeric fragments which interact with neighbouring units through K···Me contacts.[9a]

Akin to ionic lattices, the supramolecular assemblies of zincates **1**, **2**, and **3** exhibit similar alkali-metal-C and Zn-C bond distances along the extended structures precluding the definition of a specific molecular unit (Table 1). Thus, **1**, **2** and **3** can be envisaged as a regular arrangement of alkali-metal and zinc cations that are held together by a combination of electron deficient M-C and Zn-C bonds and also medium-long M···Me interactions. Moreover the $M-CH_2$ (M = Li, Na, K) distances in

1-3 are similar to those observed in monometallic alkyl species containing bridging monosilyl groups.[15,16,18,20,21,27]

Interestingly, despite the remarkable structural variations observed between **1-3**, these zincates share some key structural features: (*i*) the environment of the Zn centres in these compounds is almost identical, binding to three alkyl ligands in a trigonal planar geometry forming strong $Zn-CH_2$ bonds, which range from 2.021(2) to 2.074(2) Å (Table 1). These distances (mean Zn-C bond length, 2.043, 2.057 and 2.047 Å for **1**, **2** and **3** respectively) are very close to those witnessed in discrete zincate molecules containing bridging monosilyl groups,[28,29] (*ii*) each methylene unit is linking an alkali-metal with a zinc centre, (*iii*) each alkali-metal forms three $M-CH_2$ bonds, completing its coordination sphere by forming

additional M···CH$_3$ electrostatic interactions. Depending on the size of the alkali-metal, the number of contacts of this type varies from 1 for Li, 2 and 3 for Na and 4 for the largest cation K. These findings can be rationalized considering the different nature of the metal-carbon bonds present in these heterobimetallic species. Thus, the shorter and more covalent Zn-C σ-interactions can be described as anchoring bonds, providing the {Zn(CH$_2$SiMe$_3$)$_3$}$^-$ foundation units for these structures, to which the alkali-metals are affixed by a combination of weaker M-CH$_2$ and M···CH$_3$ ancillary bonds.[30] These long-medium Me···M interactions must greatly contribute to the overall stability of the alkali-metal zincate, by providing coordinative saturation to the unsolvated alkali-metal cations. Furthermore in **1-3**, it appears that the alkali-metal plays a major role in dictating the overall supramolecular assembly formed, which in order to maximize the number of stabilizing Me···M contacts favours different aggregation modes for the monomeric {MZn(CH$_2$SiMe$_3$} units.
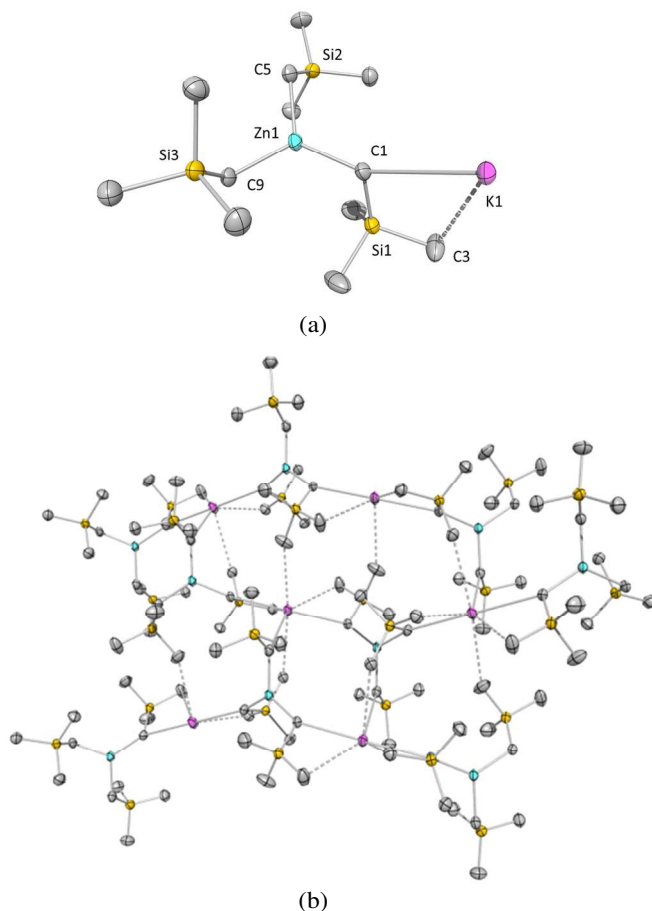

(a)

(b)

Figure 3. Solid state structure of **3** with thermal ellipsoids at 50% probability. Hydrogen atoms are omitted for clarity; (a) asymmetric unit; (b) View of the polymeric structure along the bc-plane.

It should be noted that homologous series of compounds in alkali-metal chemistry of the same formulation tend to be rare, as the fundamental differences between these metals when moving from Li to K,[31] usually favour the formation of compounds with different stoichiometries containing variable

amounts of donor molecules.[32] In zincate chemistry, Hanusa has previously reported a series of Li, Na and K triallylzincates.[11] Contrasting with the highly aggregated structures of **1-3**, these species exhibit a monomeric arrangement where the alkali-metals π-engage with the double bonds of the allyl ligands. As mentioned before the number of solvent-free triorganozincates structurally characterized is very limited. A close precedent to **1-3** is the potassium tri(cyclopentadienyl)zincate reported by Carmona which forms a 2D network connected through η^1(π) and η^5(π) coordination of three cyclopentadienyl groups to each zinc and potassium respectively.[12] In a similar fashion, the heteroleptic fortuitous compounds [KZn(CH$_2$SiMe$_3$)$_2$Ph] and [NaZnEt$_2$Ph], generated by metallation of benzene in an attempt to crystallize the parent homoleptic species from benzene solutions,[9a,13] exhibit supramolecular structures, where the alkali-metal are also stabilized by the formation of non-covalent π interactions with the phenyl groups.

When the tridentate nitrogen donor ligand PMDETA is added to lithium zincate **1**, deaggregation of its 1D polymeric arrangement is accomplished yielding monomeric zincate **4**. Exhibiting an open structural motif, where Li and Zn are connected by a single bridging alkyl group (Figure 4), the structure of **4** contrasts with that recently reported by Stalke for the methyl analogue [(PMDETA)LiZnMe$_3$], where two of the three alkyl groups attached to Zn bind to Li, closing a four-membered {LiCZnC} ring.[9d] This difference can be attributed to the larger steric demand of the CH$_2$SiMe$_3$ groups in comparison to the Me substituents, which must greatly hinder the formation of a second Li-C bond with the already tetracoordinated Li center in **4**. Supporting this interpretation, the structure of **4** bears a strong resemblance to that recently reported by our group for lithium magnesiate [(PMDETA)LiMg(CH$_2$SiMe$_3$)$_3$],[33] which can be described as an intermediate between a solvent separated ion-pair arrangement and the classical closed four-membered ring motif typically found in contacted-ion pair magnesiates. As shown in Table 1, the Zn-C bond distance of the bridging alkyl group is only marginally elongated (Zn1-C5, 2.061(2) Å) than those observed for the terminal alkyls (2.049(2) and 2.041(2) Å for Zn1-C1 and Zn1-C9 respectively). Consistent with our previous interpretation of the bonding in these heterobimetallic systems, while all Zn-C bond distances in **4** show very little deviation from those observed in highly aggregated parent zincate **1** (ranging from 2.021(2) to 2.056(2) Å), the coordination of the tridentately bonded ligand PMDETA to Li results in, not only the formation of a monomeric species, but also the noticeable elongation of the Li-C bond in **4** (2.388(4) Å *versus* 2.241 Å, average value of Li-CH$_2$ bonds in **1**). The distorted tetrahedral geometry of Li in **4** is very similar to that reported within monomeric [(PMDETA)LiCH$_2$SiMe$_3$], although as the monosilyl group binds terminally to Li, a stronger bond is formed as evidenced by its significantly shorter Li-C bond distance (2.113(2) Å).[34]
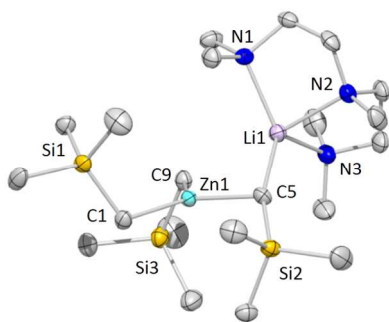
Figure 4. Solid state structure of **4** with thermal ellipsoids at 30% probability. Hydrogen atoms and disorder are omitted for clarity. Selected bond distances (Å) and angles (°): Zn1–C1 2.041(2), Zn1–C5 2.061(2), Zn1–C9 2.049(2), Li–C5 2.388(4), Li1–N1 2.133(3), Li1–N2 2.196(3), Li1–N3 2.166(4), C1-Zn1-C5 123.01(8), C1-Zn1-C9 120.61(8), C5-Zn1-C9 116.37(8), N1-Li1-C1 122.1(2), N1-Li1-N2 83.6(1), N1-Li1-N3 119.3(1), N2-Li1-C1 101.4(1), N2-Li1-N3 85.3(1), N3-Li1-C1 118.6(1).

Monomeric sodium magnesiate **5** was obtained by reacting **2** with 2 molar equivalents of diamine TMEDA. In this case, the increase on the size of the alkali-metal led to the formation of a ring-closed contacted ion pair motif (Figure 5) where the doubly chelated cation $\{(TMEDA)_2Na\}^+$ binds to two monosilyl groups. Following the trend previously mentioned for **4**, the three different Zn-C bond distances in **5** are very similar (ranging from 2.035(3) to 2.055(3) Å) and show very little variation to those found for unsolvated zincates **1-3** (see Table 1 for details). Contrastingly, the distorted octahedral Na cation in **5** forms remarkably elongated Na-C bonds (3.022(3) and 3.029(3) Å) than those in parent polymeric $[NaZn(CH_2SiMe_3)_3]$ (**2**) (average Na-CH_2 bond length, 2.678 Å).
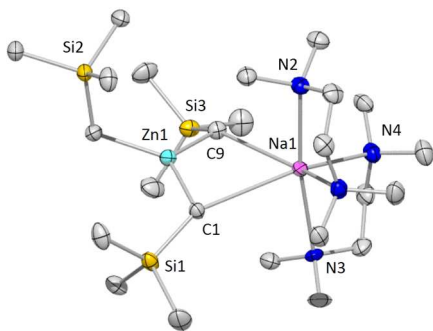

Figure 5. Solid state structure of **5** with thermal ellipsoids at 30% probability. Hydrogen atoms and minor disorder components are omitted for clarity. Selected bond distances (Å) and angles (°): Zn–C1 2.053(3), Zn1– C5 2.035(3), Zn1–C9 2.055(3), Na1–C1 3.022(3), Na1–C9 3.029(3), Na1–N1 2.565(3), Na1–N2 2.519(2), Na1–N3 2.64(1), Na1–N4 2.62(1), C1-Zn1-C5 122.1(1), C1-Zn1-C9 117.2(1), C5-Zn1-C9 120.7(1), C1-Na1-C9 70.82(8), C1-Na1-N1 90.79(8), C9-Na1-N4 91.6(3), N1-Na1-N4 111.5(3), N2-Na1-N3 172.0(2).

NMR Studies

Complementing their solid-state characterization, zincates **1-5** have also been examined in C_6D_6 using multinuclear (^{1}H and ^{13}C) NMR spectroscopy (see Table 1 and Experimental Section). Contrasting with their lack of solubility in hexane, all new zincates **1-3** show similar good solubilities in C_6D_6 to those observed for monomeric species **4** and **5**, suggesting that their polymeric constitutions observed in the solid state are not

retained in solution. Table 1 compares the informative chemical shifts observed for the M-CH_2 groups in the ^{1}H and ^{13}C NMR spectra of these zincates with those belonging to the homometallic components in the same deuterated solvent. Reflecting their bimetallic constitution, the values found for compounds **1-5** (ranging from -0.85 to -1.27 ppm in the ^{1}H NMR spectra) lie between those observed for the more polarised alkali-metal precursors (ranging from -2.03 to -2.60 ppm) and $Zn(CH_2SiMe_3)_2$ (-0.63 ppm). Furthermore, consistent with the formation of zincate anions, and therefore the generation of a new Zn-C bond, these chemical shifts are significantly closer to those found for the neutral Zn dialkyl component, a trend that has been previously found in mixed-metal chemistry for related alkali-metal zincates and magnesiates.[23d,33,35] An interesting alkali-metal effect is observed in the chemical shifts of the M-CH_2 protons **1-3**, which appear increasingly upfield when moving from Li to K (changing from -1.11 ppm for **1** to -1.16 and -1.27 ppm for **3**, Table 3 and Figure S20 in Supporting Information].[36] For zincates **1**, **2**, **4** and **5**, a single set of signals is observed for the CH_2SiMe_3 groups in the ^{1}H and ^{13}C NMR spectra, indicating a rapid exchange of the alkyl positions or alternatively the formation of solvent-separated ion pair (SSIP) solution species. Variable temperature ^{1}H NMR experiments of **1** and **2** in deuterated toluene solutions show that even at temperatures as low as 213K, the equivalence of the monosilyl groups is maintained. Notwithstanding, the noticeable differences between the chemical shifts observed for the M-CH_2 groups in the ^{1}H and ^{13}C NMR spectra of **1**, **2**, **4** and **5** (Table 3) suggest that contacted ion-pair (CIP) structures should be present in solution. Contrastingly, using the oxygen-donor polar solvent $[D_8]THF$, with a much greater coordination ability than C_6D_6, the NMR spectra recorded for **1**, **2** and **3** were almost identical,[37] being consistent with the formation of SSIP $[\{M([D_8]THF)_x\}^+\{Zn(CH_2SiMe_3)_3\}^-]$ species.

Table 3. Selected chemical shifts (ppm) in the ^{1}H and ^{13}C NMR spectra of the standards $M(CH_2SiMe_3)$ (M= Li, Na, K) and $Zn(CH_2SiMe_3)$ and new zincates **1–5** in C_6D_6 solution.

Compound	δ(^{1}H) (CH_2)	δ(^{13}C) (CH_2)
$Li(CH_2SiMe_3)$	-2.03	-4.4
$Na(CH_2SiMe_3)^a$	-2.44	
$K(CH_2SiMe_3)^a$	-2.60	
$Zn(CH_2SiMe_3)_2$	-0.63	3.2
$[LiZn(CH_2SiMe_3)_3]$ (**1**)	-1.11	1.6
$[NaZn(CH_2SiMe_3)_3]$ (**2**)	-1.14	2.9
$[KZn(CH_2SiMe_3)_3]$ (**3**)	-1.16, -1.27	4.1[b]
$[(PMDETA)LiZn(CH_2SiMe_3)_3]$ (**4**)	-0.92	2.4
$[(TMEDA)_2NaZn(CH_2SiMe_3)_3]$ (**5**)	-0.84	2.7

[a]Low solubility and poor stability of $M(CH_2SiMe_3)$ (M = Na, K) precluded the acquisition of meaningful ^{13}C NMR spectra.[b]Coincidental overlap of two different signals.
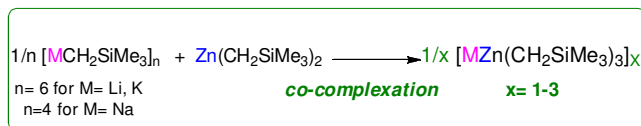
The CIP constitutions of these heterobimetallic species become more evident for heavier alkali-metal derivative **3**. According to its structure in the solid state (considering only its asymmetric unit, Figure 3a),[38] their NMR spectra at room temperature,

show two different types of alkyl groups in a 2:1 ratio (see ESI). Rapid interconversion between the two alkyl groups was observed at 313K, indicating that dynamic exchange process for this compound **3** must be higher in energy than those observed for compounds **1** and **2**, which take place at room temperature.

An interesting trend was observed when the values of the chemical shifts observed in the ^{1}H NMR spectra for the $Zn-CH_2$ groups belonging to the Lewis base adducts **4** and **5** were compared with those found for their unsolvated analogues **1** and **2** respectively. Consistent with their solid state structures, which show significantly weaker contacts between the alkali-metal and the alkyl ligands, the monosilyl groups in **4** and **5** appear at noticeable downfield chemical shifts (-0.92 ppm for **4**, $\Delta\delta(CH_2)$ **4** *vs* **1**= 0.19 ppm; -0.84 for **5**; $\Delta\delta(CH_2)$ **5** *vs* **2**= 0.3 ppm); and therefore closer to the signal observed for $Zn(CH_2SiMe_3)_2$ (-0.63 ppm).[39]

DFT Studies

To attempt to understand better the formation of zincates **1-3** in the absence of a donor solvent, we carried out a theoretical study on the co-complexation reactions between $M(CH_2SiMe_3)$ and $Zn(CH_2SiMe_3)_2$. DFT calculations were performed employing the B3LYP functional[40] and the 6-311G** basis set (for full details see Supporting Information) for the formation of **1-3**. The resultant optimized geometries were subjected to a frequency analysis. The total energy taken from the DFT calculation was adjusted by inclusion of the zero-point energy contribution. According to their donor-free structures, $LiCH_2SiMe_3$ and $NaCH_2SiMe_3$ were modelled as hexamer[18] and tetramer[15] respectively. Since the structure of donor-free KCH_2SiMe_3 has not yet been forthcoming, here it was modelled as a hexamer, as this is a commonly observed aggregation state in potassium chemistry.[41] $Zn(CH_2SiMe_3)_2$ was modelled as a monomer.[42]

$$1/n\ [MCH_2SiMe_3]_n\ +\ Zn(CH_2SiMe_3)_2\ \longrightarrow 1/x\ [MZn(CH_2SiMe_3)_3]_x$$

n= 6 for M= Li, K
n=4 for M= Na

co-complexation   x= 1-3

M= Li	X	ΔE (kcal/mol)
I-Li	1	-1.11
II-Li	2	-4.94
III-Li	3	-7.23

M= Na	X	ΔE (kcal/mol)
I-Na	1	-2.20
II-Na	2	-7.81
III-Na	3	-10.38

M= K	X	ΔE (kcal/mol)
I-K	1	-2.82
II-K	2	-8.91
IIIK	3	-10.95

Scheme 4. Relative Energies of modelled DFT Reactions to yield alkali-metal zincates **I-M**, **II-M** and **III-M** (M = Li, Na, K).

When the alkali-metal zincates were modelled as monomers, the minimum energy structures found for the products of these co-complexation reactions display a similar motif to that described for the TMEDA-sodium zincate **5**, where both metals are connected by two bridging alkyl groups, with the alkali-metal attaining further stabilization forming two additional long distance $M\cdots CH_3$ interactions with a Me from the $SiMe_3$ tail of each of the monosilyl bridges (Scheme 4, Figure 6*i*). These processes were calculated to be modestly exergonic (by -1.11, -

2.20 and -2.82 for **I-Li**, **I-Na** and **I-K** respectively), revealing very little influence on the alkali-metal employed. Interestingly, when these heterobimetallic products were modelled as dimers and trimers (Scheme 4, Figure 6*ii* and 6*iii*), the reactions became significantly more energetically favoured (by -4.94, -7.81 and -8.91 for **II-Li**, **II-Na** and **II-K** and -7.23, -10.38 and -10.95 for **III-Li**, **III-Na** and **III-K** respectively).

In close agreement to the infinite polymeric structure described for **1**, **III-Li** adopts a linear arrangement, in which two different types of four-membered rings alternate; namely {LiCZnC} rings made up by two bridging alkyl groups which connect the metals through their CH_2 groups, and {CSiCLi} rings resulting from the ambidentate coordination of the remaining type of alkyl group attached to Zn which coordinates to the Li of another {LiZn(CH₂SiMe₃)₃} monomer using its methylene unit and one of its Me groups (Figure 6 *iii*). Table 4 compares the calculated mean M-C bonds for models **I-Li**, **II-Li** and **III-Li** with the relevant experimental values obtained from the X-ray crystallographic studies of **1**. The calculated Zn-C bond distance for the three oligomers agree favourably with those found experimentally (see Supporting Information for full details). Although the strength of the $Li-CH_2$ and $Li\cdots CH_3$ interactions are slightly overestimated in the monomer **I-Li** and **II-Li**, when considering trimer **III-Li,** where the environments of the lithium centres match more closely to that described in the 1D polymeric structure of **1** (Figure 3*iii*), there is an excellent agreement for these calculated geometrical parameters and those determined experimentally [mean $Li-CH_2$ bond length, 2.198 (calc) *vs* 2.241 (exp); mean $Li-CH_3$ bond length 2.515 (both calc and exp)].[43]

Table 4. Comparison of the calculated Metal-Carbon bond distances (mean values, Å) for models **I-Li**, **II-Li** and **III-Li** with those from the X-ray crystallographic data from **1**.

Structure	mean $Zn-CH_2$	mean $Li-CH_2$	mean $Li-CH_3$
1	2.043	2.241	2.515
I-Li	2.073	2.091	2.390
II-Li	2.067	2.171	2.484
III-Li	2.065	2.198	2.515

Collectively these theoretical studies show that these co-complexation reactions become progressively more thermodynamically driven as the degree of aggregation in the newly generated heterobimetallic increases. Thus, considering the infinite supramolecular arrangements that zincates **1-3** exhibit in the solid state, judging by the trends observed in these calculations, it can be expected that their formation will be even more energetically favoured.[44] A subtle alkali-metal effect has also been revealed, as the formations of the relevant sodium and potassium zincates are, in all cases, slightly more exergonic that those computed for their lithium analogs (Scheme 4). However, it should also be noted that although different models for the **II-M** and **III-M** (M= Na and K) were calculated, the linear motif previously described for **II-Li** and **III-Li** was found to be the most thermodynamically stable (see Supporting Information for details).
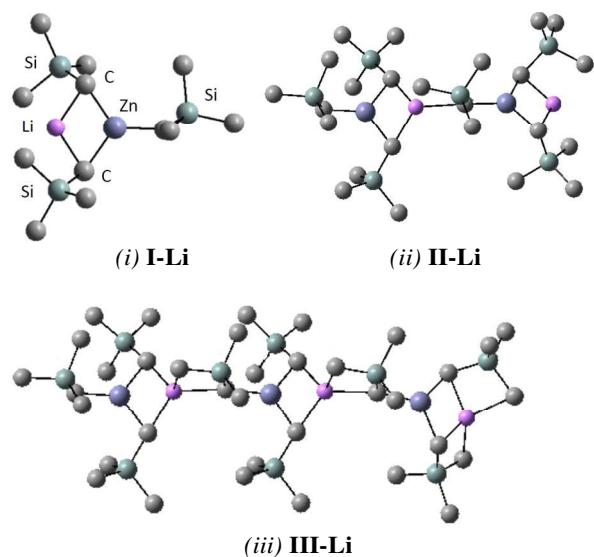
(i) **I-Li**   *(ii)* **II-Li**

(iii) **III-Li**

Figure 6. Modelled structures of lithium zincates: **I-Li** (*i*), **II-Li** (*ii*) and **III-Li** (*iii*).

Conclusions

By systematically study the co-complexation reactions of equimolar amounts of the relevant alkali-metal monosilyl MCH_2SiMe_3 (M= Li, Na, and K) with $Zn(CH_2SiMe_3)_2$ in non-coordinating hexane, the isolation and characterization of a homologous series of solvent-free triorganozincates $[MZn(CH_2SiMe_3)_3]$ (M = Li **1**, Na **2**, K **3**) has been realised. X-ray crystallographic studies have revealed the structural variations of these heterobimetallic species which exhibit intricate unprecedented supramolecular arrangements made up exclusively of a combination of M-CH_2, Zn-CH_2 and M···Me interactions. Revealing an important alkali-metal effect, lithium derivative **1** displays a linear chain structure; whereas sodium and potassium zincates **2** and **3** form much more complex 3D and 2D networks respectively. These significant differences can be explained considering the larger size and the coordinative unsaturation of these heavier alkali-metals, favouring highly aggregated assemblies, in order to maximise the number of M···CH_3 long-distance contacts. Despite the structural diversity of **1-3**, they shared the same trigonal planar $\{Zn(CH_2SiMe_3)_3\}^-$ anchor. Minimal variations were observed for the values of the Zn-C bond distances in these zincate species, which provide the foundations for their supramolecular assemblies; whereas the alkali-metals affix to these frameworks via M-CH_2 and M···CH_3 ancillary bonds. Addition of the polidentate N-donor ligands PMDETA and TMEDA (2 equivalents) to **1** and **2** respectively, cleave the highly aggregated structures of these zincates, affording monomeric $[(PMDETA)LiZn(CH_2SiMe_3)_3]$ (**4**) and $[(TMEDA)_2NaZn(CH_2SiMe_3)_3]$ (**5**). Multinuclear NMR studies of these novel zincates in deuterated benzene solutions revealed that although the supramolecular structures of **1-3** are not retained and smaller monomeric aggregates are formed, these species still maintain a contacted ion-pair constitution. New theoretical insights have been gained by modelling the co-complexation reactions of MCH_2SiMe_3 and $Zn(CH_2SiMe_3)_2$ using DFT calculations, which show that the formation of highly aggregated structures is key for thermodynamically favouring the formation of these solvent-free zincates.

Experimental section

Full experimental compounds **1-5** and computational details are included in the Supporting Information. CCDC 996623-996627 contain the supplementary crystallographic data of 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.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: CIF files giving crystallographic results and experimental and computational details. See DOI: 10.1039/b000000x/

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39. Chelating ligands PMDETA and TMEDA remain coordinated to the alkali-metal when zincates **4** and **5** respectively are dissolved in deuterated benzene as indicated by the different chemical shifts observed for the resonances belonging to this N- ligands with those observed for the free Lewis bases in C$_6$D$_6$.

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41 See for example: P. C. Andrews, A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts, R. B. Rowlings, *Angew. Chem. Int. Ed.* 2000**, 39**, 1960.

42 Although neutral Zn(CH$_2$SiMe$_3$)$_2$ has not been structurally defined, X-ray crystallographic studies of related dialkylzinc compounds containing sterically demanding substituents have demonstrated their monomeric constitution, see for example reference 19 and: (a) M. Westerhausen, B. Rademacher, W. Schwarz, J. Weidlein, S. Henkel, *J. Organomet. Chem.* 1994, **469**, 135. (b) J. Lewiński, M. Dranka, W. Bury, W. Śliwiński, I. Justyniak, J. Lipkowski, *J. Am. Chem. Soc.* 2007, **129**, 3096.

43 The outer lithium center in the hexanuclear chain **III-Li** interacts with two Me groups from the bridging monosilyl ligands. See Supporting Information for a detail list of the calculated geometrical parameters.

44 Attempts to model the dimeric and trimeric structures of **II-M** and **III-M** according to the complex 3D and 2D polymeric networks that zincates **2** and **3** display in the solid state proved unsuccessful, as some of the additional M··C stabilizing interactions, observed by X-ray crystallographic studies, could not be considered due to their high computational requirements.

Graphical Abstract

2D network of M-CH$_2$,
Zn-CH$_2$ and M···CH$_3$ bonds
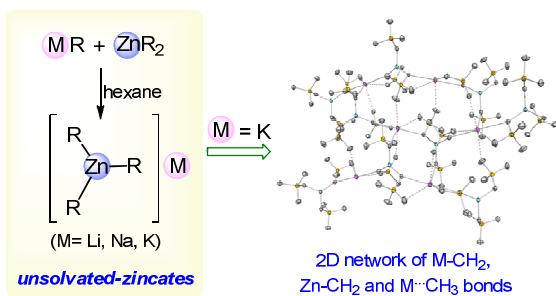
Text for TOC

Exhibiting unprecedented supramolecular assemblies, made up exclusively of metal-carbon interactions, the structures of a homologous series of solvent-free alkali-metal zincates have been uncovered.