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Lithium Dimethyl(amido)zinc Complexes: Contrasting Zincate (Amido = TMP) and Inverse Zincate (Amido = HMDS) Structures on Addition of TMEDA

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Summary: Introducing TMEDA to the lithium dimethyl(amido)zincates "$LiZn(NR_2)Me_2$" leads to a discrete ion-contacted zincate with TMEDA bound to lithium in the case of NR_2 = TMP but to a novel "inverse zincate" with TMEDA bound to zinc in the case of NR_2 = HMDS, where unexpectedly Me_2Zn(TMEDA) functions as a η^1,μ ligand to dimeric $(LiHMDS)_2$ molecules to afford a zigzag chain polymer.

Although the first alkali-metal zincate was reported as long ago as 1858,[1] through the synthesis of sodium triethylzincate ($NaZnEt_3$), this family of compounds has since gone unnoticed for long periods of time. It has only been relatively recently that synthetic chemists have started to appreciate their versatility as reagents for effecting many different chemical transformations, such as deprotonative metalation, metal−halogen exchange, and nucleophilic addition.[2] Heteroleptic zincates of the general formula $[M^+ZnR_2(X)^-]$, a special subgroup of this family, are particularly interesting, as they offer the possibility of reacting either through the R or the X ligand toward the substrate.[3] Pioneering work by Kondo has shown that lithium di-*tert*-butyl(TMP)zincate (TMP = 2,2,6,6-tetramethylpiperidide), empirically formulated as $[LiZn(TMP)(^tBu)_2]$, is an excellent chemoselective base for directing the zincation of a range of functionalized aromatic substrates.[4] The same author has found that the reactivity of these mixed-metal lithium dialkyl(amido)zincates is dramatically dependent on the specific ligands bonded to zinc.[5] Therefore, by changing the amido or alkyl group, it is possible to modulate the regioselectivity of these tunable reagents. However, no structural details of these synthetically useful zincates have been reported in these studies. The first dialkyl(amido)zincate, $[(TMTA)Li(\mu\text{-HMDS})Zn(CH_2SiMe_3)_2]$ (HMDS = 1,1,1,3,3,3-hexamethyldisilazide; TMTA = 1,3,5-trimethyl-1,3,5-triazine),[6] was reported by Westerhausen, while we recently communicated the first (TMP)zincate in the butyl-based $[(TMEDA)Li(\mu\text{-TMP})(\mu\text{-Bu})Zn(Bu)]$ (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[7] and showed that it can be used for the selective monozincation of ferrocene.

Herein we report the synthesis and structure of a new methyl-based (TMP)zincate in $[(TMEDA)Li(\mu\text{-TMP})(\mu\text{-Me})Zn(Me)]$ (**3**). The influence of the amide ligand bonded to zinc has also been probed. Thus, in an attempt to prepare the analogous lithium (HMDS)zincate of **3**, $[\{Li_2(HMDS)_2(Me)_2Zn(TMEDA)\}_\infty]$ (**4**) was obtained, which remarkably constitutes the first example of a mixed lithium−zinc but "non-zincate" (in the conventional sense) compound. Intriguingly, having TMEDA bound to Zn and not to Li, and having a trianionic coordination about Li and not about Zn, this complex could alternatively be regarded as an "inverse zincate".

The methodology employed to prepare these compounds was the same as that previously described for other dialkyl(amido)zincates (Scheme 1).[7] A solution of dimethylzinc was added to a solution of the relevant lithium amide (LiTMP or LiHMDS) in nonpolar hexane. Mixed-metal complexes are immediately formed, as indicated by the formation of extremely insoluble products, which contrasts with the high hexane solubility of their homometallic components. NMR (^{1}H, ^{13}C, and ^{7}Li) spectroscopic characterization of these solids established the formation of the unsolvated zincates $[LiZn(NR_2)Me_2]$ (where NR_2 = TMP (**1**), HMDS (**2**)) (see Experimental). This is a surprising result, as it shows that the presence of a Lewis base solvent is not required in these specific cases for inducing cocomplexation. In contrast, previous work in our laboratory shows that no such cocomplexation is accomplished with the same lithium amides when the more bulky $^tBu_2Zn$ is employed, which emphasizes the critical importance of the dialkylzinc reagent used. Though zincate **1** (generated in situ in neat THF solvent) has been described previously as a versatile reagent for generating 3-substituted benzynes,[8] it has not been isolated nor characterized in its own right. To prepare a crystalline form of **1**, we added to it 1 molar equiv of the chelating diamine TMEDA (Scheme 1). Thus, the new TMEDA-stabilized zincate **3** was produced as colorless crystals (in an isolated yield of 45%) and characterized by NMR spectroscopy, which corroborates the formation of a mixed-metal complex. Its ^{1}H NMR spectrum in C_6D_6 solution shows a singlet at −0.42 ppm corresponding to the Me groups. This chemical shift is comparable to that of uncomplexed dimethylzinc in the same solvent (−0.52 ppm), indicating that the methyl groups, although part of a lithium−zinc cocomplex, retain much of their original "zinc" bonded character.

As determined by X-ray crystallography, the structure of the ion-contacted zincate **3** (Figure 1) can be described as a four-membered LiNZnC ring (counting an agostic Li⋯Me contact), where the two metals are primarily connected by a strong TMP

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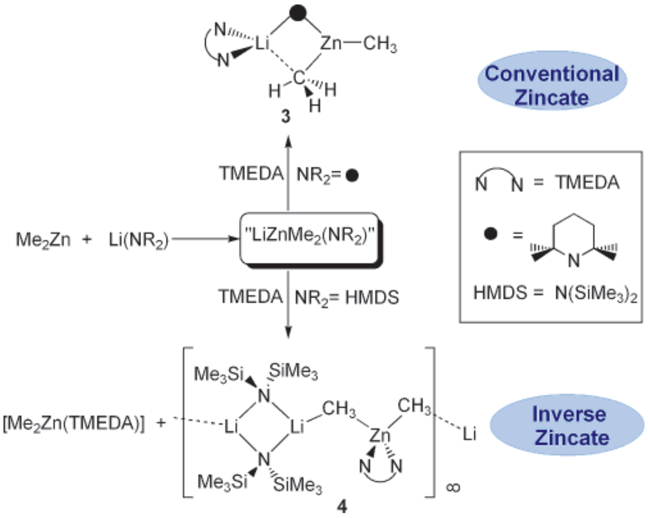
10.1021/om060334i CCC: $33.50

Scheme 1



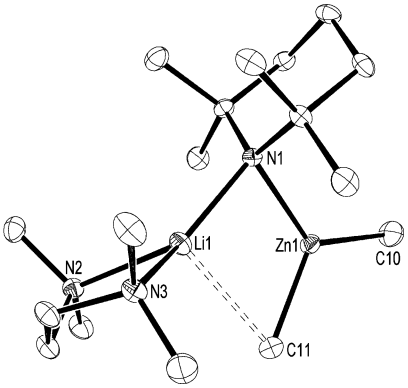


Figure 1. Molecular structure of **3** with hydrogen atoms omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

bridge which bonds equally to both (Li1$-$N1 = 2.044(4) Å, Zn1$-$N1 = 2.0482(19) Å). This TMP-bridge interaction appears to be retained when compound **3** is dissolved in arene solvents, as shown by its ^{13}C NMR spectrum in C_6D_6, where two different types of Me resonances for the TMP ligand can be assigned (see the Experimental Section). An additional secondary (agostic) interaction (Li1$\cdots$C11 = 2.603(5) Å) involving one methyl group (the other methyl group is terminal on Zn) connects the two metals. As a result, the Li center occupies a slightly pyramidal geometry (sum of N$-$Li$-$N angles 353.06°) and the N1$-$Zn1$-$C11 angle (111.93(11)°; cf. N1$-$Zn1$-$C10 = 126.55(10)°) has to become narrower to facilitate the Li$\cdots$CH$_3$ agostic interaction. This secondary weaker interaction is not present in C_6D_6 solution at ambient temperature, as both the ^{1}H and ^{13}C NMR spectra of **3** show a single resonance for both methyl groups.

By the same procedure as for **3**, TMEDA was added to a suspension of [LiZn(HMDS)Me$_2$] (**2**) in hexane, to give a solution which deposited colorless crystals when placed in the freezer. An X-ray diffraction study identified these crystals as **4** (Figure 2). This compound can be envisaged as an adduct of two neutral molecules, dimeric (LiHMDS)$_2$ and monomeric [Me$_2$Zn(TMEDA)]. LiHMDS is known to form such dimers in the presence of more conventional donors such as pyridine[9] or 1,2-dimethoxyethane.[10] The surprising donor molecule here, the formally coordinatively saturated [Me$_2$Zn(TMEDA)],[11] which is known discretely in the crystalline state, links the Li atoms to each other through a novel LiC(H$_3$)ZnC(H$_3$)Li arrangement (Li1$-$C8 = 2.382(4) Å; Li2*$-$C7 = 2.368(4) Å), to propagate a polymeric chain arrangement (Figure 3). The zigzag shape of the chain is imposed by the C$-$Zn$-$C angle (132.06(11)°), while the Zn$-$C$-$Li and C$-$Li$\cdots$Li units are slightly distorted from linearity (average Zn$-$C$-$Li angle 169.08°, average C$-$Li$\cdots$Li angle 172.49°). The Li$-$C bonds of **4** are remarkably shorter than those in **3** (2.603(5) Å) and are more comparable with those found in [{LiMe(THF)}$_4$] (mean Li$-$C distance 2.240 Å),[12] which contains methyl anions.

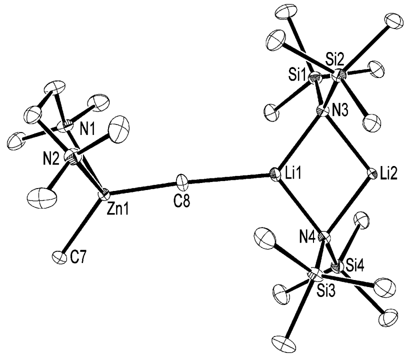


Figure 2. Asymmetric unit of **4** with hydrogen atoms omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

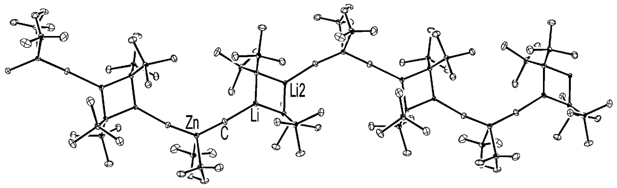


Figure 3. Section of the extended zigzag chain structure of **4**.

As a consequence of both methyl groups in **4** bridging to lithium, the Zn$-$C bond distances (2.002(2) and 2.008(2) Å) are slightly more elongated than in the monomer [Me$_2$Zn(TMEDA)][11] (1.989(9) and 1.974(9) Å). On the other hand, in contrast to the case for **3**, where the Zn is in a trigonal-planar coordination sphere (sum of the bond angles around Zn 359.98°), in **4** it assumes a distorted-tetrahedral environment, bonding to two methyl groups and the two TMEDA nitrogen atoms, while the lithium atoms are now in trigonal-planar geometries (sums of the bond angles: around Li1, 359.90°; around Li2, 358.85°). The Li$-$N bond lengths (average 2.020 Å) are in the same range as those found in other dimeric [Li(HMDS)]$_2$ structures with different monodentate ligands such as pyridine[9] and 1,4-dioxane.[10] Significantly, this intimates that the coordination of the [Me$_2$Zn(TMEDA)] moiety through the formation of strong Li$-$C bonds does not affect the basic geometric parameters of the Li(HMDS)$_2$ core of the molecule. On a search of the Cambridge Structural Database,[13] nine TMEDA-complexed lithium$-$zinc structures were found, and in every case TMEDA is bonded to lithium, not to zinc as found here.

In view of this feature, **4** can be described as an unprecedented example of a mixed-metal lithium$-$zinc complex which is a

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non-zincate. To explain, in general terms an ate compound can be described as a bimetallic system in which one metal exhibits a greater Lewis acidity than another and so is able to accept more anionic (Lewis basic) ligands. Thus, **3** can be regarded as a zincate formed by dimethylzinc (Lewis acid) and the more ionic LiTMP (a Lewis base). Within **4**, these Lewis acid/base roles are reversed, with Me_2Zn now acting as a Lewis base through the Me groups that bond to the lithium centers, while $(LiHMDS)_2$ acts as the Lewis acid counterpart. Thus, in coordination terms **4** can be described as a "lithiate" or an "inverse zincate", where each lithium engages to three anionic ligands, carrying then a partial negative charge, while the zinc center is solely bonded to two methyl groups and the neutral Lewis base TMEDA, thus having in effect a partial positive charge, reversing the normal charge distribution within a conventional zincate.

Does the solid-state structure of **4** bear any relevance to its structure in solution? On the basis of NMR spectroscopic evidence, the answer appears to be yes. Thus, while the ^1H resonance of the Me_2Zn unit in **4** (in C_6D_6 solution) appears at the same chemical shift value (−0.52 ppm) as that of "free" $Me_2Zn\cdot TMEDA$, that of the LiHMDS unit shows a significant shift from free LiHMDS (i.e., 0.28 versus 0.12 ppm). When LiHMDS is added to a solution of **4**, the HMDS resonance is found to move to 0.20 ppm, intermediate between that of **4** and pure LiHMDS, indicative of a fast exchange process between the two species. When the ^1H NMR spectrum of **4** is rerecorded in d_8-THF solution, the resonance of the LiHMDS "unit" is concident with that of free LiHMDS. From these observations it can be concluded that the LiHMDS and $Me_2Zn\cdot TMEDA$ units of **4** remain linked in C_6D_6 benzene solution but that the link is severed in strongly coordinating THF solution.

Considering that the lithium zincate $[LiZn(HMDS)Me_2]$ (**2**) is formed in hexane prior to adding TMEDA, we attribute the formation of the inverse zincate **4** to the cleavage of **2**, when the diamine is introduced, into its homometallic components, Li(HMDS) and $ZnMe_2$(TMEDA), which must recombine to form **4**. Thus, the presence of TMEDA on the Zn must activate the methyl groups, increasing their nucleophilicity such that now the zinc compound can behave as a bidentate donor through these methyl groups, with each of them bonded to a lithium center, in constructing **4**. The structure of **4** resembles that of $[\{(LiHMDS)_2(dioxane)\}_\infty]$,[10] described as a polymer of dimers of $(LiHMDS)_2$ interconnected through η^1,μ-dioxane molecules. Hence, in **4** $[ZnMe_2(TMEDA)]$ mimics the role of dioxane.

On the other hand, when TMEDA is added to $[LiZn(TMP)Me_2]$ (**1**), the expected TMEDA-solvated zincate **3**, where the diamine is more normally coordinated to the more strongly electropositive metal, lithium, is obtained. This can be rationalized, at least in part, in terms of the greater basicity of LiTMP versus LiHMDS. Thus, the Zn−N bonds in **1** must be stronger than in **2**, and therefore **1** must be a more robust zincate, resilient to cleavage in the presence of TMEDA.

In conclusion, adding TMEDA to the heteroleptic zincates $[LiZn(NR_2)Me_2]$ gives rise to two fundamentally different types of mixed lithium−zinc complexes. When NR_2 = TMP, the amidodialkyl zincate **3** is obtained with TMEDA bound to Li; however, when NR_2 = HMDS, an unprecedented inverse zincate is obtained, as the conventional Li/Zn roles within a zincate are inverted, with TMEDA now bound to Zn.

Experimental Section. The reactions were carried out in a Schlenk tube under a protective argon atmosphere.

Synthesis of $[LiZn(NR_2)(Me)_2]$ (1, 2). The relevant $Li(NR_2)$ was prepared in situ by reaction of BuLi (2.5 mL of a 1.6 M solution in hexane, 4 mmol) and the parent amine $NR_2(H)$ (4 mmol) in hexane. Me_2Zn (2 mL of a 2 M solution in toluene, 4 mmol) was then introduced. A white precipitate formed immediately in each case that was isolated by filtration and washed with hexane. Yield of **1**: 0.83 g, 86%. A few drops of deuterated THF were added to help to dissolve **1** in C_6D_6. ^1H NMR (400 MHz, 25 °C, C_6D_6): 1.87 (m, 2H, H_γ TMP), 1.47(m, 4H, H_β TMP), 1.29 (s, broad, 12H, Me TMP), −0.33 (s, 6H, Zn−CH_3). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, C_6D_6): 53.67 (C_α, TMP), 40.90 (C_β, TMP), 35.68, 33.42 (CH_3, TMP), 20.49 (C_γ, TMP), −6.53 (Zn−CH_3). ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 pppm): 0.85. Yield of **2**: 0.85 g, 81%. ^1H NMR (400 MHz, 25 °C, C_6D_6): 0.14 (s, 18H, HMDS), −0.67 (s, Zn−CH_3, Me). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, C_6D_6): 5.51 (HMDS), −6.67 (Zn−CH_3, Me). ^7Li NMR (155.50 MHz, 25 °C, C_6D_6, reference LiCl in D_2O at 0.00 ppm): 0.46.

Synthesis of [(TMEDA)Li(μ-TMP)(μ-Me)Zn(Me)] (3). To a suspension of **1** (4 mmol) in hexane, prepared in situ, TMEDA (0.60 mL, 4 mmol) was added. The resulting pale yellow solution was concentrated by removal of some solvent in vacuo and placed in the freezer at −26 °C. A crop of colorless crystals was deposited overnight. Yield of first batch: 0.64 g, 45%. ^1H NMR (400 MHz, 25 °C, C_6D_6): 1.91 (m, 2H, H_γ TMP), 1.85 (s, 16H, CH_3, TMEDA and H_β TMP), 1.78 (s, 4H, CH_2, TMEDA), 1.23 (s, 12H, Me TMP), −0.42 (s, 6H, Zn−CH_3). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, C_6D_6): 57.60 (CH_2, TMEDA), 53.62 (C_α, TMP), 47.28 (CH_3, TMEDA), 39.06 (C_β, TMP), 35.85, 34.81 (CH_3, TMP), 20.44 (C_γ, TMP), −5.84 (Zn−CH_3). ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 ppm): 0.69.

Synthesis of $[Li_2(HMDS)_2(Me)_2Zn(TMEDA)]$ (4). To a suspension of **2** (4 mmol) in hexane, prepared in situ, was added TMEDA (0.60 mL, 4 mmol). The resulting colorless solution was concentrated by removal of some solvent in vacuo and placed in the freezer at −26 °C. A crop of colorless crystals was deposited overnight. Yield of first batch: 0.52 g, 24% (note that the maximum yield possible is only 50%). ^1H NMR (400 MHz, 25 °C, C_6D_6): 1.81 (s, 12H, CH_3, TMEDA), 1.63 (s, 4H, CH_2, TMEDA), 0.28 (s, 36H, HMDS), −0.52 (s, 6H, Zn−CH_3). $^{13}C\{^1H\}$ NMR (100.63 MHz, 25 °C, C_6D_6): 57.24 (CH_2, TMEDA), 46.71 (CH_3, TMEDA), 6.28 (HMDS), −8.30 (Zn−CH_3). ^7Li NMR (155.50 MHz, C_6D_6 reference LiCl in D_2O at 0.00 pppm): 0.98. Analysis of the filtrate of the reaction confirmed that the coproduct of the reaction was $[Me_2Zn(TMEDA)]$.

Crystal data for 3: $C_{17}H_{40}LiN_3Zn$, M_r = 358.83, orthorhombic, space group *Pbca*, $a = 15.4404(4)$ Å, $b = 14.5893(5)$ Å, $c = 18.4586(5)$ Å, $V = 4158.1(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.146$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 1.182$ mm^{-1}, $T = 123$ K, 38 776 reflections were collected, 4757 reflections were unique, $R_{int} = 0.0686$, final refinement to convergence on F^2 with all non-H atoms anisotropic gave $R = 0.0414$ (F, 2833 obsd data only) and $R_w = 0.0806$ (F^2, all data), GOF = 1.006, 211 refined parameters. H atoms involved in agostic contacts were refined isotropically, but all other H atoms were placed in calculated positions and with riding modes. The maximum and minimum residual electron densities were 0.321 and −0.316 e Å^{-3}.

Crystal data for 4: $C_{20}H_{58}Li_2N_4Si_4Zn$, M_r = 546.31, monoclinic, space group $P2_1/c$, $a = 11.3371(3)$ Å, $b = 19.7104(5)$ Å, $c = 15.9168(4)$ Å, $\beta = 103.807(2)°$, $V = 3453.98(15)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.051$ g cm^{-3}, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 0.863$ mm^{-1}, $T = 123$ K, 11 205 reflections were collected, 7725 reflections were unique, $R_{\text{int}} = 0.0249$, final refinement to convergence on F^2 with all non-H atoms anisotropic gave $R = 0.0362$ (F, 5965 obsd data only) and $R_w = 0.0863$ (F^2, all data), GOF = 1.028, 306 refined parameters. H atoms involved in agostic contacts were refined isotropically, but all other H atoms were placed in calculated positions and with riding modes. The maximum and minimum residual electron densities were 0.319 and −0.316 e Å^{-3}.

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Supporting Information Available: CIF files giving crystal data for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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