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Notes

Synthesis and Structures of Solvent-Separated Lithium Zincates of the Type $[Li(tmeda)_2]^+[Me_{3-n}Zn\{CH(SiMe_3)Ph\}_n]^-$ ($n = 1-3$, tmeda = 1,2-Bis(dimethylamino)ethane)

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Summary: The reaction of methyllithium with the tmeda complex of ((trimethylsilyl)benzyl)zinc chloride in the presence of 1,2-bis(dimethylamino)ethane (tmeda) in 2:1 molar ratio quantitatively yields the heteroleptic zincate $[Li(tmeda)_2]^+[Me_{3-n}Zn\{CH(SiMe_3\}Ph]_n]^-$ *(n = 1,* ***1****). Under similar conditions, MeLi and ((trimethylsilyl)benzyl)lithium react with bis((trimethylsilyl)benzyl)zinc to form the zincates with n = 2 (****2****) and 3 (****3****), respectively. The molecular structures of* ***1*** *and* ***2*** *show shorter Zn−C bond lengths to the methyl group than to the benzylic substituent.*

The first structurally investigated zincates were solvent-free dilithium tetramethylzincate[1] and potassium trimethylzincate.[2] Whereas $Li_2[ZnMe_4]$ exists without complexation of the lithium cations by neutral Lewis bases (coligands), lithium tris[bis(trimethylsilyl)methyl]zincate[3] only forms in the presence of neutral coligands, thus forming ion-separated ion pairs. In the absence of Lewis bases, the dissociation into alkyllithium and dialkylzinc occurs. Similar results were obtained for calcium bis{tris[bis(trimethylsilyl)amino]zincate},[4] which is isolable in good yield if the calcium dication is surrounded by neutral coligands such as 1,2-dimethoxyethane. The structure of this zincate anion with the countercation $[(12\text{-crown-}4)_2Na]^+$ has been published by Dehnicke and co-workers.[5] Due to electrostatic repulsion of the three negatively charged amide substituents, long Zn−N bond lengths of 1.97 Å were observed. On the other hand, the chelating tmeda base leads to the decomposition of the zincate $[(thf)_6Mg][Zn(CH_2Ph)_3]_2$ into the corresponding neutral dibenzyl derivatives of magnesium and zinc.[6] In contrast to this finding, the addition of a tetradentate amine base to an equimolar mixture of dimethylmagnesium and dimethylcadmium yielded the solvent-separated trimethylcadmate and $MeMg[14N4]^+$.[7]

If the zinc-bonded groups contain donor atoms, intramolecularly coordinating ligands and contact ion pairs of zincates were observed.[8,9] In contrast to these observations, the zincates of sodium and potassium do not need to be stabilized by neutral coligands. Thus, Purdy and George[10] were able to isolate solvent-free sodium and potassium tris((trimethylsilyl)methyl)zincate as well as the heteroleptic potassium phenylbis((trimethylsilyl)methyl)zincate.

The presence of chelating Lewis bases such as tmeda results in the formation of solvent-separated lithium organyl zincates as can be seen from the metathesis reaction of $ZnCl_2$ with 2 equiv of $(tmeda)LiCH(SiMe_3)Ph$[11] yielding $[(tmeda)_2Li]\ [\{Ph(Me_3Si)CH\}_2ZnCl]$, which is insoluble in nonpolar solvents. On adding toluene, LiCl precipitates and the tmeda complex of homoleptic bis[phenyl(trimethylsilyl)methyl]zinc is formed.[12] The intermediate heteroleptic $ClZn(tmeda)CH(SiMe_3)Ph$ can be isolated by reacting equimolar amounts of $(tmeda)LiCH(SiMe_3)Ph$ and $ZnCl_2$.[13] The reaction of this compound with 2 equiv of methyllithium yields the

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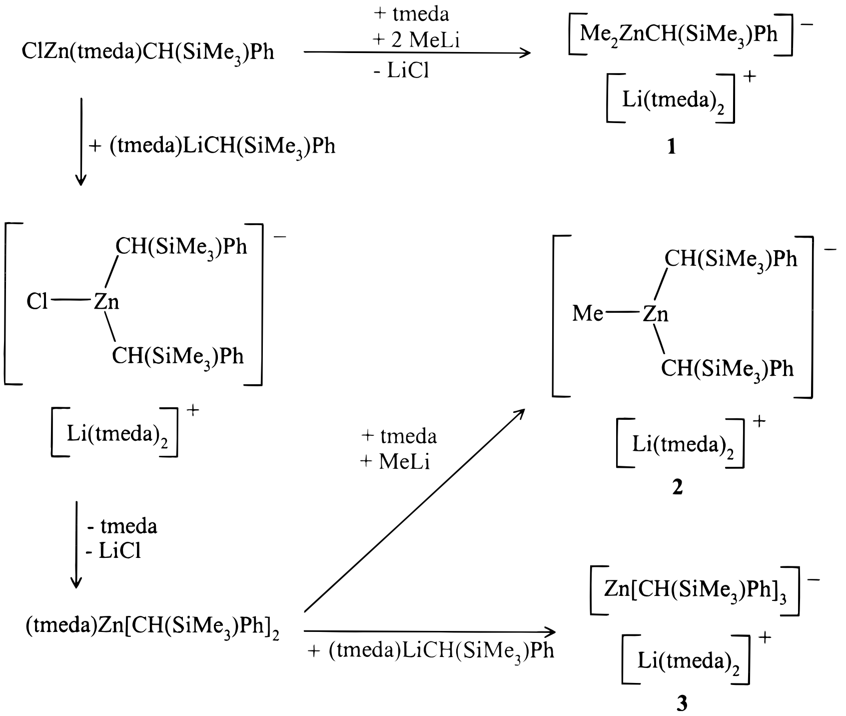
Scheme 1



zincate [Li(tmeda)$_2$] [Me$_2$ZnCH(SiMe$_3$)Ph] (**1**). The homoleptic complex (tmeda)Zn[CH(SiMe$_3$)Ph]$_2$ reacts with methyllithium/tmeda or (tmeda)LiCH(SiMe$_3$)Ph to form [Li(tmeda)$_2$] [MeZn{CH(SiMe$_3$)Ph}$_2$] (**2**) and [Li(tmeda)$_2$] [Zn{CH(SiMe$_3$)Ph}$_3$] (**3**), respectively (Scheme 1).

The thermal stability of the new zincates of the type [Me$_{3-n}$Zn{CH(SiMe$_3$}Ph]$_n$]$^-$ increases with the number *n* and the steric shielding of the central ZnC$_3$ moiety. Compound **1** already decomposes at 35 °C, whereas **3** melts at 202 °C. The sensitivity toward moisture and air decreases with increasing *n* due to increasing steric shielding of the ZnC$_3$ moiety.

The solvent-separated zincate anions of **1** and **2** contain trigonal-planar-coordinated zinc atoms. The molecular structure of the anion [Me$_2$ZnCH(SiMe$_3$)Ph]$^-$ **1** and the numbering scheme are shown in Figure 1. Figure 2 shows the anion [MeZn{CH(SiMe$_3$)Ph}$_2$]$^-$ of **2**. The cation {(tmeda)$_2$Li}$^+$ displays no unusual structural features and, therefore, it is not depicted. The Li−N bond lengths (2.082(6)−2.158(6) Å) are normal.

The zincate anion of **1** shows a rather strong distortion of the trigonal-planar coordination sphere at the zinc atom. The Zn−C bond lengths to the methyl groups are approximately 0.1 Å shorter than to the (trimethylsilyl)benzyl substituent. Furthermore, the largest bond angle (126.8(3)°) is observed for C(2)−Zn−C(3) between the methyl groups. The negative charge located mainly on the benzyl ligand leads to a shortening of the C(1)−Si(11) bond length (1.824(4) Å) compared to the Si(11)−C(11m) distances (mean value 1.872 Å). The angle C(11)−C(1)−Si(11) is widened to a value of 120.8(3)°. With these structural features, the Zn−CH(SiMe$_3$)Ph moiety of the zincate **1** displays structural parameters between those of the corresponding lithium salt, where the lithium atom bonds side-on to the benzyl fragment,[11] and the tmeda complex (tmeda)Zn[CH(SiMe$_3$)Ph]$_2$.[12] In a highly simplified view, this anion can be regarded as coordination of a benzyl anion to a molecule of dimethylzinc.

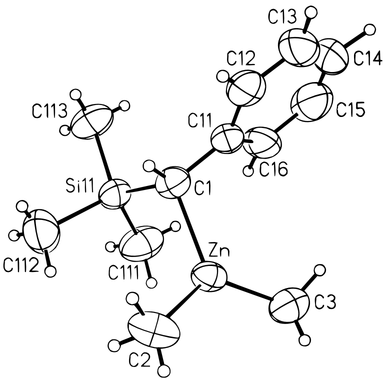


Figure 1. Molecular structure and numbering scheme of the zincate anion [Me$_2$ZnCH(SiMe$_3$)Ph]$^-$ of **1**. The ellipsoids represent a probability of 50%. Selected bond lengths (Å): Zn−C1 2.113(4), Zn−C2 2.005(5), Zn−C3 2.011(5), C1−Si11 1.824(4), C1−C11 1.470(6), C1−H1 96(4), Si11−C111 1.874(5), Si11−C112 1.864(5), Si11−C113 1.877(4). Bond angles (deg): C1−Zn−C2 113.8(2), C1−Zn−C3 119.3(2), C2−Zn−C3 126.8(3), Zn−C1−Si11 107.0(2), Zn−C1−C11 109.6(3), Si11−C1−C11 120.8(3).

The zincate anion **2** shows an even shorter Zn−C(3)$_{\mathrm{Me}}$ bond length of 1.989(8) Å. The Zn−C distances to the methyl and to the (trimethylsilyl)benzyl substituents differ by approximately 0.1 Å. The smallest CZnC bond angle is observed between the sterically demanding benzyl groups. Figure 2 shows that the hydrogen atoms are oriented in such a manner as to minimize the intramolecular steric strain.

A dependence between the bond length and the opposite bond angle was already observed for complexes with a zinc atom with a coordination number four[13,14]

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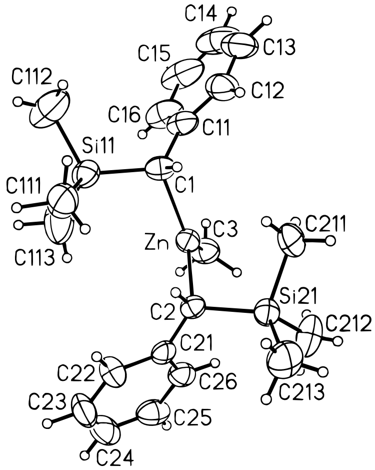

Figure 2. Molecular structure and numbering scheme of the zincate anion $[\mathrm{MeZn\{CH(SiMe_3)Ph\}_2}]^-$ of **2**. The ellipsoids represent a probability of 50%. Selected bond lengths (Å): Zn−C1 2.089(6), Zn−C2 2.084(5), Zn−C3 1.989(8), C1−Si11 1.828(7), C1−C11 1.476(8), C1−H1 87(5), C2−Si21 1.838(6), C2−C21 1.488(8), C2−H2 85(5). Bond angles (deg): C1−Zn−C2 115.2(3), C1−Zn−C3 125.1(3), C2−Zn−C3 119.7(3), Zn−C1−Si11 106.9(3), Zn−C1−C11 110.6(4), Si11−C1−C11 118.4(5), Zn−C2−Si21 106.2(3), Zn−C2−C21 107.7(4), Si21−C2−C21 122.5(4).

and for zinc bis(thiolates).[15] This concept that a lengthening of a Zn−X distance widens the opposite Y−Zn−Y angle at the zinc center nearly regardless of the size of the ligands seems to be valid, in general, as also shown for the methylbis(2,2,4,4,6,6-hexamethyl-2,4,6-trisilacyclohexyl)zincate anion.[8] However, the Zn−C distances differ by only 0.05 Å. This observation allows the conclusion that a better charge delocalization within the carbanionic ligand leads to a lengthening of the corresponding Zn−C bond length.

^{1}H NMR data show a low-field shift of the methyl as well as methine proton signals on going from **1** to **2**. For **3**, a further low-field shift is observed for the α-CH fragments. Due to the chiral α-carbon atom, two or three sets of signals were obtained for **2** and **3**, respectively. The ^{13}C{^{1}H} NMR spectra display the opposite trend for the carbon atoms bonded to the zinc center. The methyl groups cause resonances at high field at $\delta = -6.70$ for **1** and at $\delta = -7.95$ and -8.53 for the two diastereomers of **2**. A ^{7}Li{^{1}H} chemical shift of 2.4 is characteristic for the cation $[\mathrm{Li(tmeda)_2}]^+$. These zincates are more reactive than the homoleptic dialkylzinc and the corresponding alkyllithium.

Experimental Section

The general working conditions and facilities are given elsewhere.[4] The starting materials $\mathrm{(tmeda)LiCH(SiMe_3)Ph}$,[11] $\mathrm{ClZn(tmeda)CH(SiMe_3)Ph}$,[13] and $\mathrm{(tmeda)Zn[CH(SiMe_3)Ph]_2}$[12] were prepared by literature procedures. IR spectra were recorded on Nujol suspensions between CsBr windows. The NMR data were collected on tetrahydrofuran-d_8 solutions at 30 °C if not otherwise stated.

$\mathbf{[Li(tmeda)_2][Me_2ZnCH(SiMe_3)Ph]}$ (1). Methyllithium (1.15 mL of a 1.6 M solution in diethyl ether) was added slowly at 0 °C to a solution of 0.70 g of $\mathrm{ClZn(tmeda)CH(SiMe_3)Ph}$ (1.84 mmol) in 25 mL of diethyl ether. After 1 h, an additional 1.15 mL of the MeLi solution was added together with 0.28 mL of tmeda (1.84 mmol). After removal of the precipitated LiCl, the solution was reduced to 10 mL. At −20 °C, 0.87 g of colorless crystalline **1** (1.75 mmol, 97%) precipitated. Decomposition occurs at temperatures ≥35 °C.

Table 1. Crystallographic Data of 1 and 2 as Well as Details of Structure Solution and Refinement Procedures

	1	2
formula	$\mathrm{C_{24}H_{53}LiN_4SiZn}$	$\mathrm{C_{33}H_{65}LiN_4Si_2Zn}$
fw	498.10	646.38
T, K	193	193
space group[16]	$P2_12_12_1$ (no. 19)	*Pbca* (No. 61)
a, Å	9.5739(3)	28.071(4)
b, Å	13.4655(6)	14.569(3)
c, Å	24.3814(9)	19.631(3)
V, Å^3	3143.2(2)	8029(3)
Z	4	8
d_{calcd}, g cm^3	1.053	1.070
μ, mm^{-1}	0.835	0.696
F(000)	1088	2816
scan range (deg)	$1.7 \leq \theta \leq 29.6$	$1.9 \leq \theta \leq 26.0$
no. of measd data	18 251	7870
no. of unique data	6506 ($R_{\mathrm{int}} = 0.045$)	7870
no. of params	347	455
wR2[a] (all data)	0.107	0.173
R1[a] (all data)	0.084	0.169
R indices[a] with $I > 2\sigma(I)$		
data	3939	3351
wR2	0.073	0.118
R1	0.041	0.065
goof *s*[b]on F^2	1.173	1.110
residual dens, e Å^{-3}	0.251; −0.178	0.342; −0.291

[a] Definition of the *R* values: $\mathrm{R1} = (\Sigma||F_o| - F_c||)/\Sigma|F_o|$; $\mathrm{wR2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

^{1}H NMR (−40 °C): δ −1.21 (Zn−Me), 1.46 (CH), −0.07 (SiMe$_3$), 7.23−5.85 (Ph). ^{7}Li{^{1}H} NMR: δ 2.14. ^{13}C{^{1}H} NMR (−40 °C): δ −6.70 (Zn−Me, br), 39.01 (CH), 2.42 (SiMe$_3$), 157.55 (*i*-C), 127.16 (*o*-C), 125.08 (*m*-C), 114.19 (*p*_C). ^{29}Si{^{1}H} NMR (−40 °C): δ −6.37. MS (70 eV, sample 323 K, R = CH(SiMe$_3$)Ph): 390 (ZnR$_2$, 70), 326 (35), 303 (90), 242 (RZnMe, 100), 227 (ZnR, 40), 116 (tmeda, 100), 94 (ZnMe$_2$, 90).

$\mathbf{[Li(tmeda)_2][MeZn\{CH(SiMe_3)Ph\}_2]}$ (2). Methyllithium (2.15 mL of a 1.6 M solution in diethyl ether) was added at 0 °C to a solution of 1.75 g of $\mathrm{(tmeda)Zn[CH(SiMe_3)Ph]_2}$ (3.44 mmol) and 0.52 mL of tmeda (3.44 mmol) in 40 mL of diethyl ether. After 12 h, the clear solution was separated from the LiCl precipitate and was reduced in vacuo to approximately 15−20 mL. At −30 °C, 1.24 g of colorless crystalline **2** (1.92 mmol, 56%) was separated. Mp: 75 °C (dec).

^{1}H NMR (2 diastereomers): δ −1.06, −1.10 (Zn−Me), 1.52, 1.48 (CH), −0.10, −0.14 (SiMe$_3$), 6.78−6.20 (Ph). ^{7}Li{^{1}H} NMR: δ 2.28. ^{13}C{^{1}H} NMR: δ −7.95, −8.53 (Zn−Me), 35.00, 34.57 (CH), 2.31, 2.20 (SiMe$_3$), 156.43 (*i*-C), 127.30 (*o*−C), 126.55, 126.41 (*m*−C), 115.75 (*p*−C). ^{29}Si{^{1}H} NMR: δ −0.95, −1.02. MS (70 eV, sample 360 K, R = CH(SiMe$_3$)Ph): 390 (ZnR$_2$, 58), 374 (ZnR$_2$ − Me, 11), 242 (RZnMe, 12), 227 (ZnR, 45), 163 (R, 38), 73 (SiMe$_3$, 75), 58 (SiMe$_2$, 100).

$\mathbf{[Li(tmeda)_2][Zn\{CH(SiMe_3)Ph\}_3]}$ (3). Anhydrous zinc chloride (0.88 g, 6.4 mmol) was added in small portions to an ice-cooled solution of 5.53 g of $\mathrm{(tmeda)LiCH(SiMe_3)Ph}$ (19.3 mmol) in 40 mL of diethyl ether. After complete addition, the solution was heated at reflux for 2 h. After removal of precipitated LiCl, the solution was cooled to −20 °C. Crystalline colorless **3** (3.41 g, 4.3 mmol, 67%) was collected. Mp: 202 °C.

^{1}H NMR (3 overlapping sets of signals): δ 1.76, 1.71, 1.66 (CH), −0.15, −0.18, −0.36 (SiMe$_3$), 6.80−6.30 (Ph). ^{7}Li{^{1}H} NMR: δ 2.39. ^{13}C{^{1}H} NMR: δ 34.34, 33.38 (CH), 2.63, 2.41,

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1.86 ($SiMe_3$), 155.42, 154.82, 154.54 (*i*-C), 127.99, 127.85, 127.73 (*o*−C), 127.33, 127.30 (*m*−C), 117.05, 116.74 (*p*−C). $^{29}Si\{^1H\}$ NMR: δ −4.32, −4.43, −4.46. MS (70 eV, sample 243 K, R = $CH(SiMe_3)Ph$): 390 (ZnR_2, 100), 227 (ZnR, 88), 163 (R, 98), 135 (90), 116 (tmeda, 70), 73 ($SiMe_3$, 66).

X-ray Crystallography. The single crystals were covered with Nujol, sealed in thin-walled capillaries, and mounted on a four-circle diffractometer with graphite-monochromated Mo Kα radiation. For **1**, a Siemens SMART-CCD area detector was used to monitor the reflections. Crystallographic parameters and details of data collection performed at −80 °C are summarized in Table 1.

All structures were solved by direct methods with the software package SHELXTL Plus[17] and refined with the program SHELXL-93.[18] Neutral atom scattering factors were taken from Cromer and Mann,[19] and for the hydrogen atoms, they were taken from from Stewart et al.[20] The non-hydrogen atoms were refined anisotropically.

The H atoms of the cations $[Li(tmeda)_2]^+$ and of the trimethylsilyl substituents of **1** and **2** were refined with a riding model under restriction of ideal symmetry at the corresponding carbon atom, however, the C−H bond lengths were refined groupwise. The hydrogen atoms at the zinc-bonded carbon atoms were refined isotropically. For **1**, the hydrogen atoms of the phenyl substituent were refined isotropically, whereas for **2**, the positional parameters of the phenyl H atoms were refined but the *U* values were restricted to the 1.2 times the size of the corresponding C atom.

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Supporting Information Available: For compounds **1** and **2**, IR data, tables of positional coordinates, bond distances, bond angles, fractional parameters of all H atoms, and thermal parameters of the non-H atoms, and stereoscopic views of the molecular structures and unit cells (20 pages). Ordering information is given on any current masthead page.

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