Synthesis and Characterization of Substituted Benzyl Zinc Derivatives – Molecular Structures of (tmeda)Li–CH(GeMe$_3$)Ph, (tmeda)Zn(CH$_2$Ph)$_2$, (tmeda)Zn[CH(SiMe$_3$)Ph]$_2$, and (tmeda)Zn[CH(SiMe$_3$)Ph]N(H)Si(SiMe$_3$)$_3$☆

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The reaction of lithium phenyl(trimethylsilyl)methanide with phenyl(trimethylsilyl)methylzinc chloride·tmeda in the presence of tmeda yields the addition product, a bis(tmeda)lithium dialkylchlorozincate. The elimination of lithium chloride leads to the formation of a tmeda adduct of bis[phenyl(trimethylsilyl)methyl]zinc. The metathesis reaction of phenyl(trimethylsilyl)methylzinc chloride·tmeda with lithium tris(trimethylsilyl)silylamide allows the isolation of the corresponding heteroleptic tmeda complex of an alkylzinc amide. The metalation of phenyl(trimethylstannyl)methane with butyllithium yields the transmetalation product benzyllithium. From the metathesis reaction of this lithium base with anhydrous zinc(II) chloride in the presence of tmeda, the tmeda adduct of dibenzylzinc crystallizes. The molecular structures of (tmeda)Li–CH(GeMe$_3$)Ph, (tmeda)Zn(CH$_2$Ph)$_2$, (tmeda)Zn[CH(SiMe$_3$)Ph]$_2$, and (tmeda)Zn[CH(SiMe$_3$)Ph]N(H)Si(SiMe$_3$)$_3$ are reported. Whereas lithium bonds in an η^3-fashion, the zinc atom forms a σ(Zn–C) bond. The extremely wide Zn–N–Si angle in (tmeda)Zn[CH(SiMe$_3$)Ph]N(H)Si(SiMe$_3$)$_3$ of 157° is remarkable.

Dialkylzinc and trialkylzincate derivatives are used as alkylating reagents and as initiators for anionic polymerization processes. The easy access and the quantitative formation of the zinc and zincate compounds allow an in situ preparation without work-up and isolation of these products. The presence of bulky ligands such as tris(trimethylsilyl)methyl[1] or the coordination of 1,2-bis(dimethylamino)ethane (tmeda) at the zinc atom[2] facilitates the isolation of heteroleptic dialkylzinc or alkylzinc chloride.[2][3] The function of coordinated tmeda as a bidentate Lewis base occupying coordination gaps and thus protecting the metal centers from the attack of substrates and from dismutation reactions is often neglected. However, this property provides a valuable method to prepare monomeric heteroleptic zinc derivatives with various alkyl and aryl substituents.[2][3]

Dibenzylzinc[4] as well as bis(trimethylsilylmethyl)zinc[5] have been well known compounds for decades. The combination of an α-trimethylsilyl and α-phenyl substitution of a methylzinc moiety leads to a chiral ligand at the zinc atom. The stepwise metathesis reaction of (tmeda)LiCH(SiMe$_3$)Ph with anhydrous zinc dichloride firstly gives (tmeda)Zn(Cl)[CH(SiMe$_3$)Ph].[2] The subsequent addition of methyllithium leads to the formation of heteroleptic (tmeda)Zn(Me)[CH(SiMe$_3$)Ph][2] without the observation of an ate complex as an intermediate. The linear dependency of the Zn–N$_{\mathrm{tmeda}}$ bond lengths on the E–Zn–E angle in (tmeda)ZnE$_2$ fragments has also been demonstrated in an earlier study[2][6] where E can be a chloride, pseudo-halide, alkyl, or phenyl ligand.

Our interest is mainly centered on the mechanism of the synthesis of (tmeda)ZnR$_2$ as well as on the preparation of an alkylzinc amide. Here we report the first X-ray crystal structure of a tmeda complex of an alkylzinc amide with a moderately bulky alkyl substituent. The chirality of the alkyl substituent leads to enantiomeric alkylzinc derivatives. In the case of dialkylzinc derivatives, diastereomers are also to be expected.

Synthesis

We are not only interested in spectroscopic and structural properties of the zinc derivatives, but also in the heavy atom effect by a formal substitution of the silicon atom of the trimethylsilyl group with germanium or tin. This is best seen for the substances of the type Ph(Me$_3$Si)C(H)MMe$_3$ (**1**). The synthesis of these derivatives is straightforward using the reaction of (tmeda)Li–CH(SiMe$_3$)Ph with the chlorides Me$_3$M–Cl of silicon, germanium, and tin according to Eq. 1. Another synthetic route has been described for **1a** by reductive coupling of H$_5$C$_6$CCl$_3$ and chlorotrimethylsilane with magnesium[7] or lithium in the presence of di-*tert*-butylbiphenyl[8] with a subsequent protolysis.

The reaction of trimethylsilyl- and trimethylgermylphenylmethane with an alkyllithium in the presence of tmeda

$$\text{(tmeda)LiCH(SiMe}_3\text{)Ph} + \text{Cl–MMe}_3 \rightarrow \text{Me}_3\text{M–CH(SiMe}_3\text{)Ph} + \text{LiCl} + \text{tmeda} \quad (1)$$

M	Si	Ge	Sn
	1a	**1b**	**1c**

yields the corresponding substituted lithium methanides **2a**[9] and **2b** (Eq. 2). However, the reaction of butyllithium with the homologous trimethylstannylphenylmethane in tetrahydrofuran leads, by a transmetalation according to Eq. 3, to the already structurally characterized benzyllithium **2c**[10], coordinated by one tmeda and one THF molecule. This transmetalation reaction is widely used[11] to obtain alkyllithiums even at very low temperatures. The advantage of this transmetalation reaction is its practicability in the absence of tmeda. Therefore, the lithiation of **1c** with an alkyllithium yields the tmeda-free lithium phenyl(trimethylsilyl)methanide, whereas for the reaction displayed in Eq. 2 the presence of tmeda in the reaction solution is necessary.

$$\text{Li}n\text{Bu} + \text{H}_2\text{C(MMe}_3\text{)Ph} + \text{tmeda} \rightarrow \text{(tmeda)Li–CH(MMe}_3\text{)Ph} + \text{HR} \quad (2)$$

M	Si	Ge
	2a	**2b**

$$\text{Li}n\text{Bu} + \text{H}_2\text{C(SnMe}_3\text{)Ph} + \text{tmeda} + \text{thf} \rightarrow \underset{\textbf{2c}}{\text{(tmeda,thf)Li–CH}_2\text{Ph}} + n\text{BuSnMe}_3 \quad (3)$$

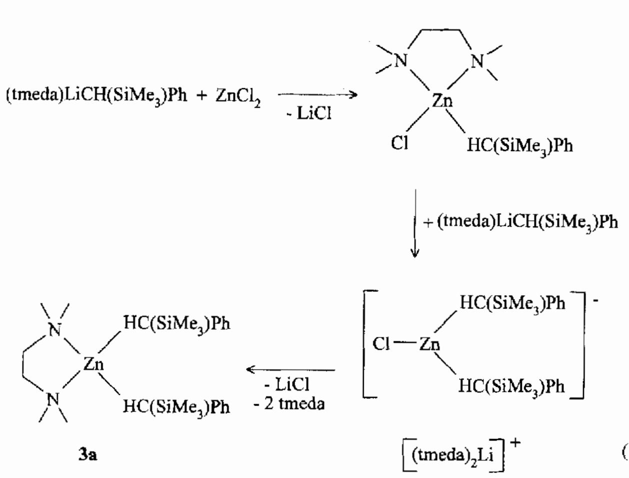
The metathesis reaction (Eq. 4) of the benzyllithium derivatives **2a-c** with anhydrous zinc dichloride yields the tmeda complexes of $\text{Zn[CH(MMe}_3\text{)Ph]}_2$ **3a** (M = Si) and **3b** (M = Ge) as well as that of dibenzylzinc **3c**, respectively.

$$2\ \text{(tmeda)Li–CH(Z)Ph} + \text{ZnCl}_2 \rightarrow \text{(tmeda)Zn[CH(Z)Ph]}_2 + 2\ \text{LiCl} + 2\ \text{tmeda} \quad (4)$$

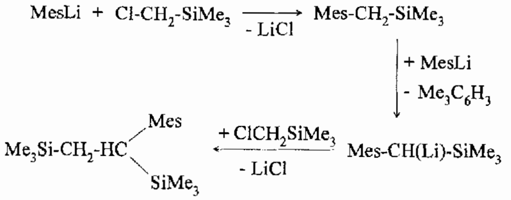
Z	SiMe$_3$	GeMe$_3$	H
	3a	**3b**	**3c**

The course of the reaction was monitored by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy for the preparation of **3a**. The first reaction step is the metathesis reaction, which was followed by the addition of (tmeda)lithium phenyltrimethylsilylmethanide **2a** to (tmeda)Zn(Cl)CH(SiMe$_3$)Ph to yield the heteroleptic zincate $[\text{(tmeda)}_2\text{Li}]^+\{\text{ClZn[CH(SiMe}_3\text{)Ph}\}^-$. Characteristic resonances for the α-CH group of the two diastereomers were detected at $\delta(^1\text{H}) = 1.48$ and 1.55 as well as at $\delta(^{13}\text{C}\{^1\text{H}\}) = 29.6$ [^1J(C,H) = 112 Hz] and 30.14 [^1J(C,H) = 110 Hz] in the ratio of 2:1 in addition to the signals of the starting materials and the product. Prolonged stirring at room temperature or, preferably, heating the reaction solution to 60 °C, accelerates the precipitation of lithium chloride and the formation of **3a**. Eq. 5 shows the reaction sequence deduced from these findings. For **3a** and **3b** two diastereomers are detected by NMR spectroscopy in benzene, whereas the enantiomers are indistinguishable in achiral solvents.

In order to obtain 2,4,6-trimethylphenyl-(mesityl-)substituted compounds, mesityllithium[12] was reacted with chlormethyltrimethylsilane to yield mesityltrimethylsilylmethane.



(5)



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(6)

However, this substance is not isolable, but it is lithiated by a second equivalent of mesityllithium and the coupling reaction with a second equivalent of ClCH$_2$SiMe$_3$ yields derivative **4**. The reaction sequence is shown in Eq. 6. Further efforts to obtain mesityltrimethylsilylmethane were not undertaken.

The equimolar use of **2a** and anhydrous ZnCl$_2$ and the subsequent reaction with lithium tris(trimethylsilyl)silylamide[13] leads to the formation of the tmeda adduct of Ph(Me$_3$Si)CH–Zn–N(H)Si(SiMe$_3$)$_3$ **5** according to Eq. 7. As early as 1965, Coates and Ridley[14] investigated heteroleptic alkylzinc amides such as dimeric ethylzinc diphenylamide as well as selected Lewis base complexes. The addition of tmeda yields the mononuclear tmeda adduct (tmeda)Zn(Et)NPh$_2$ as determined by a cryometric determination.[15] Monomeric alkylzinc amides RZn–NR′R″ are also stabilized by bulky substituents R at the zinc atom such as the tris(trimethylsilyl)methyl group.[1][2] However, dismutation of **5** is observed during the removal of the tmeda ligand by the mass spectroscopic detection of homoleptic bis[phenyl(trimethylsilyl)methyl]zinc.

$$\text{(tmeda)ClZn–CH(SiMe}_3\text{)Ph} + \text{LiNHSi(SiMe}_3\text{)}_3 \rightarrow$$
$$\underset{\textbf{5}}{\text{Ph(Me}_3\text{Si)CH–(tmeda)Zn–NHSi(SiMe}_3\text{)}_3} + \text{LiCl} \quad (7)$$

NMR Spectroscopy

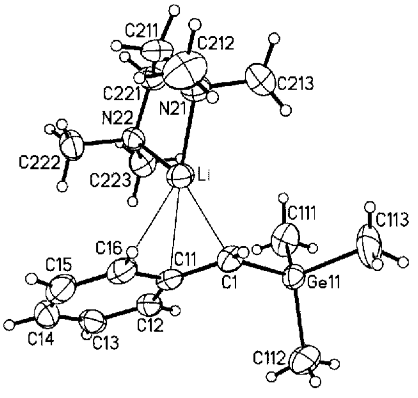
The comparison of selected NMR parameters obtained from [D$_6$]benzene solutions at room temperature is shown in Table 1 for the derivatives **1** to **3** and **5**. The chemical shifts of the ^{29}Si{^{1}H} nuclei depend strongly on whether another trimethylsilyl group (approximately 2 ppm), a lithium (−15 ppm), or a zinc atom (−1 ppm) is bonded to the

Table 1. Comparison of the NMR data of the alkyl substituents of the derivatives **1**–**5** (chemical shifts [ppm], coupling constants [Hz])

	HR[a]	**1a**	**1b**	**1c**	**2a**[b]	**2b**	**2c**[c]	**3a**	**3b**	**3c**	**5**
^{1}H:											
δ(CH)		1.40	1.53	1.69	1.87	2.03	1.61	1.32	1.39	1.58	1.31
δ(SiMe$_3$)		0.02	0.03	0.04	0.36			0.32			0.19
δ(GeMe$_3$)			−0.20			0.45			0.35		
^{13}C:											
δ(α-C)	27.5	29.8	29.4	25.5	41.7	42.9	37.1	29.5	28.9	21.2	26.2
^1J(Si,C)		42.9	45.8	47.1	78.0						
^1J(C,H)	121	107	113	116	126	131	131	108	113	120	101
δ(SiMe$_3$)	−1.8	0.5	0.1	0.2	2.7	1.7		1.7	0.9		1.5
^1J(Si,C)		51.4	51.3	51.3	48.6			50.1			
δ(*i*-C)	140.6	143.0	143.9	144.9	156.5	157.7	161.2	151.3	152.9	153.9	152.2
δ(*o*-C)	128.6	128.5	128.5	128.2	118.7	117.8	116.9	130.0	129.7	128.2	129.0
δ(*m*-C)	128.6	129.9	128.6	128.6	130.1	130.0	128.4	128.1	129.1	126.6	128.2
δ(*p*-C)	124.5	123.9	123.8	123.3	109.2	108.4	104.7	121.0	120.8	119.2	120.5
^{29}Si{^{1}H}:											
δ(Si)		1.6	2.0	2.3	−15.1			−0.9			2.2

[a]R = CH(SiMe$_3$)Ph, see literature[16]. – [b]Identical with data in ref.[9]. – [c]See ref.[10]. – [d]Only one diastereomer is listed, see Experimental Section.

Figure 1. Molecular structure and numbering scheme of **2b**; thermal ellipsoids are drawn at a 50% probability level; the hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Li–C1 213.7(5), Li–C11 227.2(5), Li–C16 263.9(5), Li–N21 206.4(5), Li–N22 202.0(5), C1–C11 142.5(4), C1–Ge11 189.7(3), Ge11–C111 195.7(3), Ge11–C112 195.2(3), Ge11–C113 195.3(3); Ge–C1–C11 126.4(2), Li–C1–C11 76.4(2), Li–C1–Ge 120.4(2).

α-carbon atom. The signals of the α-carbon atoms show a low-field shift of δ = 21–43 depending on the nature of the substituents. For PhCH$_2$SiMe$_3$ a ^{13}C{^{1}H} chemical shift of δ = 27.5[16] is observed for the methylene group. Whereas the NMR data for the trimethylsilyl-substituted compounds **1** and the zinc derivatives **3** are rather similar, the lithium derivatives **2** display some characteristic features. The high-field shift of the silicon signal has already been mentioned and, furthermore, the extremely large coupling constant ^1J(Si,C) of 78 Hz is remarkable. The ^1J(C,H) values vary between 107 and 120 Hz for **1** and **3**, whereas for **2** larger values around 130 Hz were observed. The effect of the change from the trimethylsilyl to the trimethylgermyl group is rather small, however, the ^1J(C,H) coupling constants are higher in the germyl derivative.

The heavy-atom effect in the list of compounds **1** is clearly seen for the α-CH moiety. The proton resonance is shifted to lower field with increasing metal size. Contrasting behavior is observed for the δ(^{13}C) value. Both the ^1J(Si,C) and ^1J(C,H) coupling constants increase in the change from the silicon derivative **1a** to the tin compound **1c**. Similar trends are valid for the tmeda complexes **3a** and **3b**.

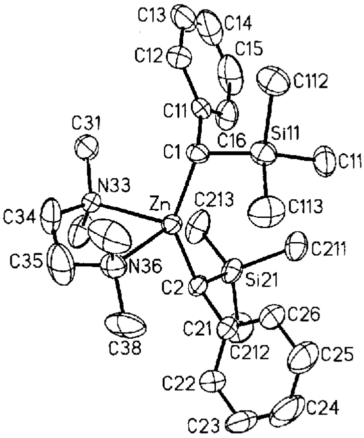
Molecular Structures

The similarities in the trimethylsilyl and trimethylgermyl derivatives are also valid for the solid state structures. **2a**[9] and **2b** crystallize isotypically with comparable Li–C and Li–N distances. Figure 1 shows the molecular structure and the numbering scheme of **2b**. The lithium atom is bonded to the bidentate tmeda ligand and side-on coordinated to the benzyl moiety, thus enforcing a small Li–C1–C11 angle of 76.4°. The Li–C bond lengths of 213.7, 227.2, and 263.9 pm lie in the region characteristic for oligomeric alkyllithium compounds.[17] The Ge11–C1–C11 angle is widened to 126.4°, however, the corresponding Si–C–C value is even larger at 129.2°.[9] Due to hyperconjugation the Ge–C1 bond length is approximately 6 pm shorter than the Ge–C bonds within the trimethylgermyl substituent. Corresponding findings were also reported for homologous **2a**.[9]

Due to the marked similarities between the silicon and the germanium derivatives **2a** and **2b**, only the structures of the zinc dialkanides **3a** and **3c** are compared. The molecular structures and the numbering schemes of **3a** and **3c** are represented in Figures 2 and 3, respectively. Due to the steric demand of the trimethylsilyl substituents an enhanced C–Zn–C angle of 141.6° is observed for **3a**. According to previous investigations[2][6] a consequence of the widening of this angle is the elongation of the Zn–N bonds to a value of 232 pm, however, the Zn–C distances are mainly established by the coordination number of the metal center and differ by only 1 pm. With a C–Zn–C angle of 122.2° for (tmeda)Zn(CH$_2$Ph)$_2$, Zn–N bond lengths of 221 pm are found in the solid state. The α-carbon atoms C1 and C2 of **3a** are in a tetrahedral environment and a widening of the

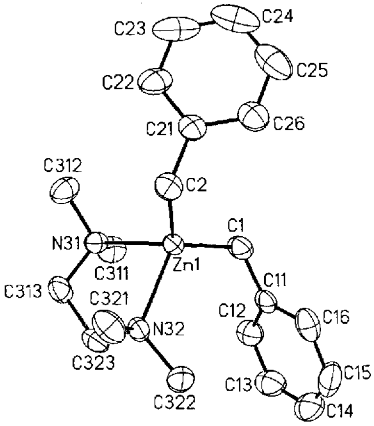
Si−C−C angles, as described for the lithium derivative **2a**[9], is not achieved. Furthermore, all the Si−C bond lengths are the same within the standard deviations. Between the α-carbon atoms and the *ipso*-carbon atom of the phenyl group there is no double-bond character whatsoever [**3a**: C(*n*)−C(*n*1) 150 pm; **3c**: C(*n*)−C(*n*1) 148 pm], whereas the lithium derivatives **2a**[9] and **2b** show a shortening of the C1−C11 bond. Due to the chirality of the alkyl substituent, three isomeric forms of **3a** are possible [(*R*,*R*), (*S*,*S*), and (*R*,*S*)] and observed by NMR spectroscopy but only the (*R*,*R*) and (*S*,*S*) isomers crystallized.

Figure 2. Molecular structure and numbering scheme of the (*R*,*R*) isomer of **3a**; thermal ellipsoids are drawn at a 40% probability level; the hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Zn−C1 204.1(4), Zn−C2 205.0(4), Zn−N33 232.9(4), Zn−N36 231.4(4), C1−C11 150.1(6), C1−Si11 186.5(5), C2−C21 150.5(6), C2−Si21 186.0(5); C1−Zn−C2 141.6(2), Zn−C1−C11 114.7(3), Zn−C1−Si11 118.6(2), C11−C1−Si11 107.9(3), Zn−C2−C21 113.3(3), Zn−C2−Si21 119.6(2), C21−C2−Si21 109.1(3).

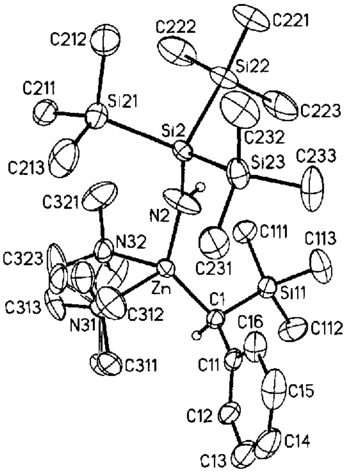
Figure 3. Molecular structure and numbering scheme of **3c**; thermal ellipsoids are drawn at a 50% probability level; the hydrogen atoms are omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Zn1−C1 203.2(4), Zn1−C2 203.9(4), Zn1−N31 220.2(3), Zn1−C32 220.9(3), C1−C1 1147.6(6), C2−C21 148.2(5); C1−Zn1−C2 122.2(2), Zn1−C1−C11 116.7(3), Zn1−C2−C21 111.5(3).

The molecular structure and the numbering scheme of the heteroleptic zinc derivative **5** is represented in Figure 4. The sterically very demanding tris(trimethylsilyl)silyl substituent forces the linearization of the Zn−N2−Si2 fragment (157.0°) and a widening of the C1−Zn−N2 angle to 127.1°. The amide proton is localized but an isotropic refinement failed. The N2−Si2 as well as the Si2−Si(2*m*) distances of the amide ligand lie in the expected region. The Zn−C1 bond length of 202.4 pm corresponds to the values discussed above. The Zn−N2 distance of 190.4 pm is longer than those found in homoleptic zinc diamides with a zinc atom of coordination number of two (characteristic value for Zn−N is 182 pm[18]). The Zn−N bond length of a bis(trimethylsilyl)amide ligand bound terminally to a triply coordinated zinc atom varies between 185 and 186 pm.[19][20][21] From this point of view the Zn−N2 bond length found in **5** is in accordance with the expected value. A higher coordination number of four at the nitrogen atom, due to a μ-coordination of the amide ligand between a zinc and another metal atom, leads to a further increased Zn−N distance of more than 200 pm.[19][22] The N2−Si2 bond length of 170.9 pm in **5** is even shorter than in the dimeric lithium amide $[LiN(SiMe_3)Si(SiMe_3)_3]_2$.[13] Due to the two sterically and electronically different anionic ligands at the zinc center, the Zn−N bonds to the tmeda molecule in **3a** and **3c** differ by approximately 7 pm.

Figure 4. Molecular structure and numbering scheme of **5**; thermal ellipsoids are drawn at a 40% probability level; the hydrogen atoms are omitted for clarity[a]



[a] The disorder within the tmeda ligand is shown; selected bond lengths [pm] and angles [°]: Zn−C1 202.4(3), Zn−N2 190.4(3), Zn−N31 218.2(3), Zn−N32 225.2(3), N2−Si2 170.9(3), Si2−Si21 237.1(1), Si2−Si22 236.1(1), Si2−Si23 236.1(1), C1−C11 149.8(4), C1−Si11 185.7(3); C1−Zn−N2 127.1(2), Zn−N2−Si2 157.0(2), Zn−C1−C11 111.7(2), Zn−C1−Si11 112.4(2), N2−Si2−Si21 118.9(1), N2−Si2−Si22 104.9(1), N2−Si2−Si23 112.8(2).

Conclusions

The reactivity of the tmeda adduct of phenyl(trimethylsilyl)methylzinc chloride was investigated. The reaction with another equivalent of (tmeda)LiCH(SiMe$_3$) yields the addition product, a chlorodialkylzincate, which could be detected by NMR spectroscopy. The elimination of lithium chloride from this zincate leads to the formation of homoleptic dialkylzinc. During the addition of a lithium amide no zincate was detected, however, due to the coordination of a tmeda molecule at the zinc atom no dismutation reactions to the homoleptic derivatives were observed. The steric repulsion between the tris(trimethylsilyl)silyl group and the neutral coligand leads to a marked widening of the Zn−N−Si angle. The removal of the tmeda ligand under vacuum allows ligand-ligand exchange reactions so that homoleptic bis[phenyl(trimethylsilyl)methyl]zinc has been found by mass spectrometry.

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Experimental Section

The general working conditions and facilities are given elsewhere.[23] The starting materials 2,4,6-trimethylphenyllithium (mesityllithium),[12] (tmeda)LiCH(SiMe$_3$)Ph (**2a**),[9] (tmeda, thf)LiCH$_2$Ph (**2c**),[10] LiN(H)Si(SiMe$_3$)$_3$[13] and Cl(tmeda)Zn[CH(SiMe$_3$)Ph]$_2$[2] were prepared by literature procedures. − IR spectra were recorded from Nujol suspensions between CsBr windows. − The NMR data were collected from [D$_6$]benzene solutions at 30 °C if not otherwise stated.

Phenylbis(trimethylsilyl)methane (**1a**), *Phenyl(trimethylgermyl)(trimethylsilyl)methane* (**1b**), *Phenyl(trimethylsilyl)(trimethylstannyl)methane* (**1c**). − *General Procedure:* A stoichiometric amount of chlorotrimethylsilane, -germane, or -stannane, respectively, was added slowly at 0 °C to a stirred solution of **2a** in diethyl ether. The precipitated lithium chloride was filtered off. The ether was removed under reduced pressure at room temp. before the residue was distilled under vacuum. The yield was at least 80% in each case.

Physical Data of **1a**: B.p. 63 °C/0.01 Torr. − ^{1}H NMR (similar data to ref.[8]): $\delta = 0.02$ (SiMe$_3$), 1.40 (CH), 6.8−7.3 (phenyl). − ^{13}C NMR: $\delta = 0.49$ [SiMe$_3$, ^{1}J(Si,C) = 51.4 Hz], 29.79 [CH, ^{1}J(Si,C) = 42.9 Hz, ^{1}J(C,H) = 107.1 Hz], 143.03 (*ipso*-C), 128.49 (phenyl), 129.91 (phenyl), 123.88 (*para*). − ^{29}Si{^{1}H} NMR: $\delta = 1.56$. − IR: $\tilde{\nu} = 1608$ cm^{-1} m, 1502 m, 1486 w, 1457 w, 1430 w, 1339 w, 1256 vs, 1206 s, 1161 w, 1074 w, 1039 s, 1001 w, 912 m, 872 sh, 846 vs, 774 m, 754 w, 739 w, 702 s, 690 m, 657 w, 616 w, 562 w, 505 w.

Physical Data of **1b**: B.p. 41 °C/0.01 Torr. − ^{1}H NMR: $\delta = 0.03$ (SiMe$_3$), 0.16 (GeMe$_3$), 1.53 (CH), 6.8−7.3 (phenyl). − ^{13}C NMR: $\delta = -0.20$ [GeMe$_3$, ^{1}J(C,H) = 125.2 Hz], 0.10 [SiMe$_3$, ^{1}J(Si,C) = 51.3, ^{1}J(C,H) = 118.7 Hz], 29.36 [CH, ^{1}J(Si,C) = 45.8 Hz, ^{1}J(C,H) = 112.6 Hz], 143.86 (*ipso*-C), 128.68 (phenyl), 128.48 (phenyl), 123.82 (*para*-C). − ^{29}Si{^{1}H} NMR: $\delta = 2.01$. − IR: $\tilde{\nu} = 1604$ cm^{-1} m, 1500 s, 1482 w, 1458 w, 1421 w, 1271 sh, 1255 vs, 1236 w, 1215 s, 1076 m, 1039 s, 912 m, 867 vs, 844 vs, 823 s, 801 w, 771 m, 756 w, 742 w, 703 s, 691 w, 642 w, 627 w, 600 vs, 570 m, 501 m.

Physical Data of **1c**: B.p. 45 °C/0.01 Torr. − ^{1}H NMR: $\delta = 0.04$ (SiMe$_3$), 0.07 (SnMe$_3$), 1.69 (CH), 6.8−7.3 (phenyl). − ^{13}C NMR: $\delta = -8.11$ [SnMe$_3$, ^{1}J(^{119}Sn,C) = 324.3 Hz), 0.21 [SiMe$_3$, ^{3}J(Sn,C) = 11.4 Hz, ^{1}J(Si,C) = 51.3 Hz], 25.45 [CH, ^{1}J(Sn,C) = 234.8 Hz, ^{1}J(Si,C) = 47.1, ^{1}J(C,H) = 115.7 Hz], 144.86 [*ipso*-C, ^{2}J(Sn,C) = 36.9 Hz], 128.63 [*meta*-C, ^{4}J(Sn,C) = 9.2 Hz], 128.19 [*ortho*-C, ^{3}J(Sn,C) = 10.8 Hz], 123.34 [*para*-C, ^{5}J(Sn,C) = 12.4 Hz]. − ^{29}Si{^{1}H} NMR: $\boldsymbol{\delta} = 2.34$ [^{2}J(Sn,Si) = 17.6 Hz]. − ^{119}Sn{^{1}H} NMR: $\boldsymbol{\delta} = 10.37$. − IR: $\tilde{\nu} = 1611$ cm^{-1} m, 1503 s, 1460 m, 1426 m, 1366 w, 1330 m, 1255 vs, 1214 s, 1190 w, 1162 s, 1061 m, 1036 w, 1017 w, 906 w, 855 vs, 774 m, 740 m, 700 vs, 675 w, 601 w, 554 w, 510 w, 473 m, 401 w.

[1,2-Bis(dimethylamino)ethane-N,N']lithium Phenyl(trimethylgermyl)methanide (**2b**): A commercially available butyllithium/hexane solution (2.5 M, 4.2 ml, 10.5 mmol) was added dropwise slowly to a solution of 2 ml of phenyltrimethylgermylmethane (10.8 mmol) and 1.44 ml of tmeda (10.8 mmol) in 20 ml of diethyl ether at room temp. After stirring overnight, the red solution was concentrated to approximetely 5 ml and cooled to −10 °C. Crystallization gave 3.21 g of red **2b** (90%), m.p. 90 °C (reversible, without decomposition). − ^{1}H NMR: $\boldsymbol{\delta} = 0.45$ (GeMe$_3$), 1.61 (CH$_2$ tmeda), 1.71 (Me tmeda), 2.03 (α-CH), 6.14 [*para*-H, ^{3}J(H,H) = 7.0 Hz, ^{4}J(H,H) = 1.2 Hz], 6.56 [*ortho*-H, ^{3}J(H,H) = 8.4 Hz]. − ^{13}C NMR: $\boldsymbol{\delta} = 1.67$ (GeMe$_3$), 42.89 [CH, ^{1}J(C,H) = 131.0 Hz], 44.56 (Me tmeda), 55.92 (CH$_2$ tmeda), 157.71 (*ipso*-C), 130.03 (phenyl), 117.83 (phenyl), 108.39 (*para*-C). − IR: $\tilde{\nu} = 1318$ cm^{-1} vs, 1296 m, 1259 vs, 1238 w, 1223 w, 1183 m, 1166 m, 1135 w, 1104 w, 1065 m, 1042 m, 1019 m, 979 s, 946 m, 849 m, 842 w, 810 s, 794 m, 773 w, 746 s, 698 vs, 615 m, 602 s, 582 m, 571 m, 541 vs, 446 w. − MS (70 eV, source 450 K, sample 330 K); *m/z* (%): 58 (100)[tmeda^{2+}], 116 (6.5) [tmeda^{+}], 119 (30.5) [GeMe$_3^{+}$], 194 (5.9) [PhCHGeMe$_2^{+}$], 210 (2.6) [PhCH$_2$GeMe$_3^{+}$] 299 (2.1). − C$_{16}$H$_{31}$GeLiN$_2$ (330.96): calcd. C 58.06, H 9.44, N 8.46; found C 58.02, H 9.64, N 8.26.

[1,2-Bis(dimethylamino)ethane-N,N']zinc Bis[phenyl(trimethylsilyl)methanide] (**3a**): A solution of 52.7 mmol of **2a** in 20 ml of diethyl ether was prepared from 10 ml of phenyl(trimethylsilyl)methane, 7.1 ml of tmeda and 21.0 ml of a 2.5 M butyllithium/hexane solution. To this solution was added 3.59 g of anhydrous zinc dichloride (26.4 mmol) in small portions. The precipitated LiCl was separated and the solution concentrated to only a few ml. Cooling to 0 °C yielded 11.2 g of crystalline **3a** (84%), m.p. 125−126 °C. The NMR data show two diastereomers in the ratio of 3:1. − ^{1}H NMR: $\delta = 0.32$ and 0.31 (SiMe$_3$), 1.32 and 1.48 (CH), 1.62 (Me tmeda), 1.68 (CH$_2$ tmeda). − ^{13}C NMR: $\delta = 1.71$ [SiMe$_3$, ^{1}J(Si,C) = 50.1 Hz], 1.91 [SiMe$_3$, ^{1}J(Si,C) = 49.9 Hz], 29.50 [CH, ^{1}J(C,H) = 107.8 Hz], 30.16 [CH, ^{1}J(C,H) = 105.0 Hz], 47.65 (tmeda), 57.64 (tmeda), 151.31 and 151.37 (*ipso*-C), 129.98 and 129.33 (phenyl), 128.09 and 128.22 (phenyl), 120.97 and 120.75 (*para*-C). − ^{29}Si{^{1}H} NMR: $\delta = -0.93$ and -0.81. IR: $\tilde{\nu} = 1598$ cm^{-1} s, 1577 w, 1295 m, 1260 m, 1245 s, 1198 vs, 1181 m, 1169 w, 1129 m, 1105 w, 1075 sh, 1068 m, 1046 w, 1033 s, 1019 m, 999 w, 946 s, 903 s, 846 vs 834 vs, 797 s, 788 s, 744 s, 703 s, 677 s, 626 w, 616 m, 575 m, 542 w, 530 m, 502 s, 474 m, 448 w, 382 w. − Raman (single crystal): $\tilde{\nu} = 1587$ cm^{-1} s, 1467 w, 1443 w, 1409 w, 1190 vs, 1173 w, 1162 w, 1147 w, 1027 s, 995 vs, 946 m, 930 m, 854 w, 809 w, 783 m, 742 w, 702 w, 683 w, 675 m, 623 w, 612 m, 596 s, 542 m, 502 w, 473 w, 379 w, 298 s, 269 w, 212 m, 169 m.

[1,2-Bis(dimethylamino)ethane-N,N']zinc Bis[phenyl(trimethylgermyl)methanide] (**3b**): 4.2 ml of 2.5 M butyllithium/hexane solution was added dropwise to 2.26 g of phenyl(trimethylgermyl)methane (10.8 mmol) and 1.44 ml of tmeda (10.8 mmol) in 20 ml of diethyl ether. After stirring for two hours at room temp., 0.74 g of anhydrous zinc(II) chloride (5.4 mmol) was added in small portions. After separation of the precipitated lithium chloride, the solution was concentrated to approximately 5 ml. Cooling of this solution to 0 °C yielded 2.64 g of **3b** (82%), m.p. 122−124 °C. The ^{13}C-NMR data showed two diastereomers in the ratio of 3:1. − ^{1}H NMR: $\delta = 0.35$ (GeMe$_3$), 1.39 (CH), 1.59 (Me tmeda), 1.62 (CH$_2$ tmeda), 6.7−7.3 (phenyl). − ^{13}C NMR: $\delta = 0.91$ (GeMe$_3$), 1.32 (GeMe$_3$), 28.86 [CH, ^{1}J(C,H) = 112.5 Hz], 29.58 [CH, ^{1}J(C,H) = 112.9 Hz], 47.54 (tmeda), 57.46 (tmeda), 152.88 and 153.33 (*ipso*-C), 129.66 and 129.07 (phenyl), 128.15 and 128.05 (phenyl), 120.75 and 120.42 (*para*-C). − IR: $\tilde{\nu} = 1598$ cm^{-1} s, 1492 s, 1294 s, 1251 m, 1241 m, 1233 m, 1228 sh, 1199 vs, 1188 m, 1168 w, 1104 w, 1066 m, 1048 s, 1032 m, 1018 w, 968 w, 956 s, 937 w, 901 w, 820 vs, 796

Table 2. Crystallographic data of **2b**, **3a**, **3c**, and **5** as well as details of the structure solution and refinement procedures

Compound	**2b**	**3a**	**3c**	**5**
Empirical formula	$C_{16}H_{31}GeLiN_2$	$C_{26}H_{46}N_2Si_2Zn$	$C_{20}H_{30}N_2Zn$	$C_{25}H_{59}N_3Si_5Zn$
Molecular mass (g·mol^{-1})	330.96	508.20	363.83	607.57
T [K]	193	193	193	193
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group[25]	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Unit cell dimensions				
a [pm]	1296.3(1)	1715.2(1)	785.7(2)	1258.2(3)
b [pm]	976.6(1)	1734.1(2)	1608.4(3)	1748.0(4)
c [pm]	1552.1(2)	1995.3(1)	1579.7(3)	1705.7(4)
β [°]	102.28(2)		96.85(3)	99.38(2)
V [nm^3]	1.9199(3)	5.9347(8)	1.9820(7)	3.701(2)
Z	4	8	4	4
$d_{\mathrm{calcd.}}$ [g·cm^{-3}]	1.145	1.138	1.219	1.090
μ [mm^{-1}]	1.589	0.923	1.241	0.842
F(000)	704	2192	776	1320
Diffractometer	Siemens P4	Siemens P4	Siemens P4	Siemens $P2_1$
Scan mode, width [°]	ω-scan, 1.2	ω-scan, 1.3	ω-scan, 1.3	Wyckoff, 1.2
Scan range [°]	$1.6 \leq \theta \leq 27.0$	$2.0 \leq \theta \leq 26.0$	$1.8 \leq \theta \leq 27.5$	$1.6 \leq \theta \leq 25.0$
Measured data	4333	5762	4861	6818
Unique data	4148	5762	4537	6513
Number of parameters	242	332	328	503
R indices[a] with $I > -\sigma(I)$				
all data	3980	5296	4227	6321
wR_2	0.1004	0.1511	0.1193	0.1085
R_1	0.0618	0.1239	0.1071	0.0581
R indices[a] with $I > 2\sigma(I)$				
data	3122	3240	2856	5291
wR_2	0.0935	0.1192	0.1053	0.0978
R_1	0.0386	0.0565	0.0525	0.0415
Goodness-of-fit s[b] on F^2	1.035	0.987	0.995	1.058
Residual density [e·nm^{-3}]	459; −635	539; −468	380; −426	458; −376

[a] Definition of the R values: $R_1 = (\Sigma\|F_o| - |F_c\|)/\Sigma F_o$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$[27]. – [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

m, 776 s, 743 m, 704 s, 655 m, 596 s, 560 m, 545 w, 528 m, 494 s, 470 m, 441 w, 274 w. – MS (70 eV, source 455 K, sample 340 K); *m/z* (%): 482 (4.0) [M^+ – tmeda], 386 (2.4), 209 (6.3) [$PhCHGeMe_3^+$], 194 (15.7) [$PhCHGeMe_2^+$], 119 (29.3) [$GeMe_3^+$], 116 (66.5) [tmeda$^+$], 105 (45.7), 58 (100) [tmeda^{2+}]. – $C_{26}H_{46}Ge_2N_2Zn$ (596.57): calcd. C 52.27, H 7.77, N 4.69; found C 52.23, H 7.53, N 4.64.

[1,2-Bis(dimethylamino)ethane-N,N']dibenzylzinc (**3c**): 7.85 ml of a 2.5 M butyllithium/hexane solution was added dropwise slowly to a solution of 5.0 g of benzyltrimethylstannane (19.6 mmol) and 2.64 ml of tmeda in 20 ml of diethyl ether. After cooling to 0 °C, 1.34 g of anhydrous zinc dichloride (9.8 mmol) was added in small portions. After complete addition, the solution was stirred for an additional 3 h at room temp. After filtration to remove lithium chloride, the solution was concentrated to approximately 10 ml. Crystallization at −10 °C afforded 2.85 g of **3c** (80%), m.p. 103 °C. – ^1H NMR: δ = 1.58 (CH_2 benzyl), 1.70 (Me tmeda), 1.82 (CH_2 tmeda), 6.8–7.3 (phenyl). – ^{13}C NMR: δ = 21.22 [CH_2, $^1J(C,H)$ = 120.4 Hz], 46.96 (tmeda), 56.76 (tmeda), 153.93 (*ipso*-C), 128.22 (phenyl), 126.56 (phenyl), 119.20 (*para*-C). – IR: $\tilde{\nu}$ = 1601 cm^{-1} s, 1307 w, 1295 m, 1253 m, 1212 vs, 1195 w, 1180 m, 1153 w, 1131 m, 1105 w, 1068 m, 1032 s, 1012 vs, 988 vs, 955 s, 940 w, 882 m, 821 w, 796 s, 771 w, 752 s, 699 s, 656 m, 626 w, 603 m, 553 w, 542 m, 534 m, 478 m, 435 m. – MS (70 eV, source 430 K, sample 295 K); *m/z* (%): 182 (25.4) [$PhCH_2CH_2Ph^+$], 91 (100) [$PhCH_2^+$].

1-(2,4,6-Trimethylphenyl)-1,2-bis(trimethylsilyl)ethane (**4**): 8.57 g of MesLi·LiBr·OEt_2 (30 mmol) was dissolved in 40 ml of tetrahydrofuran; 5 ml of chlormethyltrimethylsilane was added slowly at room temp. Precipitated solid material was separated and the solution distilled under vacuum. 3.77 g of **4** (86%) were obtained at 78 °C/0.01 Torr. – ^1H NMR: δ = −0.14 ($SiMe_3$), 0.01 ($SiMe_3$), 2.24 (*ortho*-Me), 2.11 (*para*-Me), 6.71 (*meta*-H), 0.90 [CH_2, $^3J(H,H)$ = 4.2 Hz, $^2J(H,H)$ = 15.2 Hz], 1.33 [CH_2, $^3J(H,H)$ = 11.9 Hz, $^2J(H,H)$ = 15.2 Hz], 2.71 [CH, $^3J(H,H)$ = 4.2 Hz, $^3J(H,H)$ = 11.9 Hz]. – ^{13}C NMR: δ = −0.86 [$SiMe_3$, $^1J(Si,C)$ = 49.9 Hz, $^1J(C,H)$ = 118.5 Hz], −0.46 [$SiMe_3$, $^1J(Si,C)$ = 50.2 Hz, $^1J(C,H)$ = 118.7 Hz], 16.72 [CH_2, $^1J(Si,C)$ = 51.8 Hz, $^1J(C,H)$ = 116.6 Hz], 20.82 [*para*-Me, $^1J(C,H)$ = 125.6 Hz], 22.55 [*ortho*-Me, $^1J(C,H)$ = 125.4 Hz], 22.67 [*ortho*-Me, $^1J(C,H)$ = 125.5 Hz], 25.42 [CH, $^1J(Si,C)$ = 49.8 Hz, $^1J(C,H)$ = 112.7 Hz], 139.54 (*ipso*-C), 135.86 (*ortho*-C), 135.09 (*ortho*-C), 133.42 (*para*-C), 130.96 (*meta*-C), 129.54 (*meta*-C). – $^{29}Si\{^1H\}$ NMR: δ = 2.24, 4.43. – IR: $\tilde{\nu}$ = 2975 cm^{-1} sh, 2954 vs, 2910 sh, 2890 sh, 2861 s, 2729 w, 1621 m, 1588 w, 1486 s, 1457 s,br, 1428 m, 1383 m, 1343 w, 1254 vs, 1229 w, 1202 w, 1172 w, 1141 m, 1108 m, 1033 m, 1016 m, 839 vvs, br, 752 s, 689 s, 615 m, 601 w, 566 w, 550 w, 519 w, 471 w, 424 w, 363 w. – $C_{17}H_{32}Si_2$ (292.615): calcd. C 69.78, H 11.02; found C 69.72, H 10.98.

[1,2-Bis(dimethylamino)ethane-N,N']zinc Phenyl(trimethylsilyl)methanide Tris(trimethylsilyl)silylamide (**5**): 1.17 g of LiN(H)-$Si(SiMe_3)_3$ (4.34 mmol) dissolved in 20 ml of diethyl ether was slowly added dropwise to a stirred solution 1.65 g of $Ph(Me_3Si)CHZn(tmeda)Cl$ (4.34 mmol) in 20 ml of diethyl ether. After 10 h, the precipitated lithium chloride was removed by filtration and the solution concentrated to a few ml. 2.32 g of colorless crystals of **5** (88%) precipitated at −10 °C, m.p. 101 °C. – ^1H NMR: δ = −0.08 (NH), 0.19 ($CSiMe_3$), 0.41 ($SiSiMe_3$), 1.31 (ZnCH), 1.70 (CH_2 tmeda), 1.80 (Me tmeda), 6.8–7.3 (phenyl). – ^{13}C NMR: δ = 1.49 ($CSiMe_3$), 1.60 ($SiSiMe_3$), 26.24 [ZnCH, $^1J(C,H)$ = 101 Hz], 47.14

(tmeda), 56.89 (tmeda), 152.24 (*ipso*-C), 129.01, 128.19, 120.49 (*para*-C). – $^{29}Si\{^1H\}$ NMR: $\delta = -0.75$ (ZnCSi), -17.21 (Si*Si*$_3$), -39.40 (*Si*Si$_3$). – IR: $\tilde{\nu} = 1588\ cm^{-1}$ s, 1484 s, 1355 w, 1291 m, 1251 sh, 1239 vs, 1202 s, 1176 w, 1164 w, 1149 w, 1128 m, 1114 m, 1065 m, 1047 w, 1030 s, 1014 m, 993 w, 952 m, 933 m, 898 s, 845 sh, 835 vs, 794 s, 784 s, 771 sh, 743 m, 703 s, 680 s, 623 m, 577 w, 544 m, 501 s, 470 m, 439 w, 386 w, 338 w, 302 w. – $C_{25}H_{59}N_3Si_5Zn$ (607.58): calcd. C 49.41, H 9.79, N 6.92; found C 48.21, H 9.93, N 6.35.

X-ray Structure Determinations[24]: The single crystals were covered with nujol, sealed in thin-walled capillaries and mounted on a four-circle diffractometer with graphite monochromated Mo-K_α radiation. Crystallographic parameters and details of data collection performed at −80 °C are summarized in Table 2. After every 98 reflections the intensity and orientation of two check reflections were measured and showed no decay. No absorption or extinction corrections were applied. All structures were solved by direct methods with the software package SHELXTL Plus[26] and refined with the program SHELXL-93.[27] Neutral atom scattering factors were taken from Cromer and Mann[28] and for the hydrogen atoms from Stewart et al.[29] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms of **2b** as well as **3c** were refined isotropically. The H atoms of **3a** 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. For **5** the hydrogen atoms of the phenyl(trimethylsilyl)methyl and tris(trimethylsilyl)silyl substituents were refined isotropically, whereas the hydrogen atoms of the tmeda ligand were calculated in ideal positions. The N-bonded H atom of **5** was found in a difference Fourier syntheses, however, the refinement failed. Therefore, this atom was fixed on the found position, and the positional parameters and the *U* value were not refined.

☆ Dedicated to Professor *Manfred Weidenbruch* on the occasion of his 60th birthday.

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