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An alkylzinc bromide and a lithium alkyldibromozincate containing tris(organosilyl)methyl groups

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Abstract

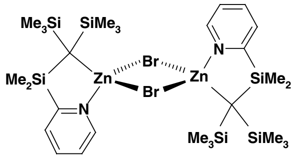
The lithium reagent $\mathrm{Li(THF)_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}}$ (**3**) reacts with a molar equivalent of anhydrous zinc bromide to give the dimeric compound $\mathrm{[Zn(\mu\text{-}Br)\{C(SiMe_3)_2(SiMe_2NMe_2)\}]_2}$ (**2a**), in which zinc is four-coordinate. The product from a similar reaction with $\mathrm{Li\{C(SiMe_3)_2(SiMe_2NPhMe)\}}$ is the lithium zincate $\mathrm{[Li(THF)_2(\mu\text{-}Br)_2Zn\{C(SiMe_3)_2(SiMe_2NPhMe)\}]}$ (**4**), in which the zinc is only three-coordinate. The crystal structures of **2a** and **4** have been determined.

Keywords: Organozinc; Organosilyl; Crystal structures

1. Introduction

Methyl- and ethylzinc iodides, prepared by Frankland in 1849 [1], played an important part in the development of organometallic chemistry and the concept of valency [2]. A number of organozinc halides have been structurally characterised as complexes with oxygen or nitrogen donors [3], but structural data on unsolvated organozinc halides are sparse. The compounds $\mathrm{[ZnClSiPhMe_2)_3\}]_2}$ [4], $\mathrm{[ZnCl\ (OEt_2)\{CCl_2CF_3\}]_2}$ [5], $\mathrm{[ZnCl\{(CH_2)_3\ NMe_2\}]_2}$ [6] and $\mathrm{[ZnBr\{C(SiMe_3)_2SiMe_2(C_5H_4N\text{-}2)\}]_2}$ (**1**) [7] form halide-bridged dimers. The crystalline iodides ZnIEt [8] and $\mathrm{ZnICH_2CH_2CN}$ [9] have polymeric structures.

We surmised that organozinc halides bearing bulky organic groups might be precursors to catalysts for ring opening polymerisation of lactide, particularly since their molecular architecture, and hence the access of substrates, can be controlled by variations in substituents within the bulky group [10].



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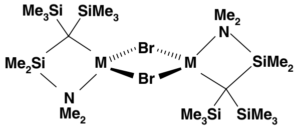
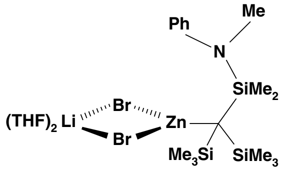


2a M = Zn **2b** M = Co



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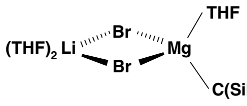

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We therefore made the compound $\mathrm{[Zn(\mu\text{-}Br)C(SiMe_3)_2(SiMe_2NMe_2)]_2}$ (**2a**) from the lithium reagent $\mathrm{Li(THF)_2\{C(SiMe_3)_2(SiMe_2NMe_2)\}}$ (**3**) [11] and a molar equivalent of zinc bromide. An attempt to make the analogous compound containing the new ligand $\mathrm{C(SiMe_3)_2(SiMe_2NPhMe)}$ in the same way led to the isolation of the lithium organodibromozincate $\mathrm{[Li(THF)_2(\mu\text{-}Br)_2Zn\{C(SiMe_3)_2(SiMe_2NPhMe)\}]}$ (**4**). Although the compounds $\mathrm{[Li(OEt_2)(\mu\text{-}X)_2ZnL]}$ (X = Cl (**5a**) or I (**5b**), $\mathrm{L = 2{,}6\text{-}Pr^i_2C_6H_3N{=}C(Me)CH{=}C(Me)}$-

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[1] Died 22.02.04. This paper is dedicated to his memory.

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$NC_6H_3Pr^i_2$-2,6) have been reported [12], compound **4** is, as far as we are aware, the first containing the $LiBr_2Zn$ core to be structurally characterised.

2. Experimental

Air and moisture were excluded as far as possible by the use of Schlenk techniques, flame-dried glassware and a nitrogen-filled drybox. NMR spectra from samples in C_6D_6 were recorded at 300.1 (^1H), 75.4 (^{13}C), 194.5 (^7Li), 50.7 (^{15}N) or 99.4 Hz (^{29}Si), with signals from quaternary ^{13}C, ^{29}Si and ^{15}N enhanced by polarisation transfer. Chemical shifts are relative to $SiMe_4$ for H, C and Si, LiCl in D_2O for Li, and $MeNO_2$ for N. EI mass spectra were obtained at 70 eV; except where indicated for M_2 (**2a**), indicated for M_2 (**2a**), *m/z* values are for ^{79}Br and ^{64}Zn.

2.1. $[\overline{ZnBr\{C(SiMe_3)_2(SiMe_2N}Me_2)\}]_2$ **(2a)**

A solution of LiMe (5.2 mmol) in Et_2O (3.2 cm^3) was added slowly to a stirred solution of $(Me_3Si)_2(Me_2NSiMe_2)CH$ [11] (1.35 g, 5.2 mmol) in THF (40 cm^3) at room temperature. The mixture was stirred for 5 h, then added dropwise to a stirred solution of $ZnBr_2$ (1.16 g, 5.2 mmol) in THF (20 cm^3) at −110 °C. The mixture was allowed to warm to room temperature and the solvents were removed under vacuum to leave a solid that was extracted with *n*-hexane. The extract was filtered and the solvent pumped from the filtrate to leave a white air- and moisture-sensitive solid that was recrystallised from heptane at 0 °C to give crystals of **2a**, m.p. 112–114 °C, suitable for an X-ray study. Anal. Calc. for $C_{22}H_{60}Br_2N_2Si_6Zn_2$: C, 32.55; H, 7.45; N, 3.45. Found: 32.47; H, 8.65; N, 3.86%. We think the low value for H is in error since none of the NMR spectra shows any evidence for impurities. ^1H NMR: δ 0.17 (6H, s, $SiMe_2$), 0.41 (18H, s, $SiMe_3$), 2.18 (6 H, s, NMe_2). ^{13}C NMR: δ 3.0 ($SiMe_2$), 7.3 ($SiMe_3$), 14.8 (CSi_3), 41.6 (NMe_2). ^{29}Si NMR: $\delta - 4.5$ ($SiMe_3$), 22.3 ($SiMe_2$). *m/z*: 812 (0.5, $C_{22}H^{79}_{60}Br^{81}BrN_2Si^{64}_6Zn^{66}Zn$, M_2), 797 (0.5, M_2–Me), 724 (5, M_2–$SiMe_4$), 659 (1, M_2–Me_3SiBr), 581 (10, M_2–Me–$(Me_3Si)_2CSiMe_2$), 499 (10, possibly M_2–MeBr–$(Me_3Si)_2CSiMe_2$), 388 (10, M–Me), 372 (20, M–Me–CH_4), 310 (5, M–Me–Br), 230 (10, $Me_2Si{=}C(SiMe_2NMe_2)SiMe_2$), 219 (30, MH–$CH_2{=}NCH_2$), 201 (100, $Me_2Si{=}C(SiMe_3)SiMe_2$), 129 (15, $Me_2Si{=}CHSiMe_2$), 73 (60, $SiMe_3$).

2.2. Preparation of $(Me_3Si)_2\{(PhMeN)Me_2Si\}CH$ *(6)*

N-methylaniline (9.0 cm^3, 83 mmol) was added dropwise to a stirred solution of $(Me_3Si)_2(Me_2BrSi)CH$ [13] (12.8 g, 43 mmol) in hexane (120 cm^3) at −78 °C. The mixture was allowed to warm to room temperature, then stirred for 2 h. The volume was reduced to 15 cm^3, the white precipitate filtered off, and solvents removed from the filtrate under vacuum. The oily residue was distilled at 88–90 °C/0.02 mmHg to give $(Me_3Si)_2\{(PhMeN)Me_2Si\}CH$ (**6**) (8.0 g, 60%). Anal. Calc. for $C_{16}H_{33}NSi_3$: C, 59.44; H, 10.22; N, 4.33. Found: C, 59.27; H, 10.40; N, 4.05%. ^1H NMR (C_6D_6): δ 0.08 (18H, s, $SiMe_3$), 0.16 (1H, s, CH), 0.32 (6H, s, $SiMe_2$), 2.64 (3H, s, NMe), 6.78 (1H, tt, $^3J_{HH} = 7.3$ Hz and 1 Hz, *p*-H), 6.85 (2H, m, *m*-H), 7.15 (2H, m, *o*-H). ^{13}C NMR: δ 3.2 ($^1J_{CH} = 118$ Hz, $^1J_{SiC} = 51$ Hz, $SiMe_3$), 3.7 ($^1J_{CH} = 119$ Hz, $^1J_{SiC} = 58$ Hz, $SiMe_2$), 4.8 ($^1J_{CH} = 97$ Hz, $^1J_{SiC} = 36.5$ and 43.5 Hz, $^3J_{CH} = 3.5$ Hz, CSi_3), 35.4 ($^1J_{CH} = 135.0$ Hz, NMe), 118.1 ($^1J_{CH} = 154.6$ Hz, *o*-C), 118.7 ($^1J_{CH} = 160.2$ Hz, *p*-C), 128.8 ($^1J_{CH} = 156.4$ Hz, *m*-C), 150.9 (*i*-C). ^{15}N NMR: −328.8. ^{29}Si NMR: $\delta - 0.9$ ($SiMe_3$), 6.6 ($SiMe_2$). MS: *m/z* 323 (50, M), 308 (50, M–Me), 217 (100, M–NMePh), 203 (30, $(Me_3Si)_2CHSiMeH$), 164 (20, $Me_2SiNMePh$), 129 (40, $Me_2Si{=}CHSiMe_2$), 73 (40, $SiMe_3$).

2.3. Reaction of $(Me_3Si)_2\{(PhMeN)Me_2Si\}CH$ with LiMe

A solution of LiMe (1.76 mmol) in Et_2O (1.1 cm^3) was added dropwise to a stirred solution of **6** (0.50 g, 1.54 mmol) in THF (15 cm^3) at room temperature. The mixture was stirred overnight, then solvent was slowly removed under vacuum. No crystals were obtained. All solvent was removed to leave a pale yellow oil, shown by NMR spectroscopy to be a 1:2 mixture of unchanged **6** and a new compound assumed to be $Li(THF)_2C(SiMe_3)_2(SiMe_2NMePh)$ (**7**). ^1H NMR (C_6D_6): δ 0.42 (18H, s, $SiMe_3$), 0.58 (6H, s, $SiMe_2$), 1.31 (8H, m, THF), 2.73 (3H, s, NMe), 3.46 (8H, m, THF), 6.5–7.3 (m, Ph). ^{13}C NMR: δ 6.85 ($SiMe_2$), 7.55 ($SiMe_3$), 25.3 (THF), 34.9 (NMe), 68.3 (THF), 115.3(*o*-C), 117.5 (*p*-C), 129.9 (*m*-C) 152.7 (*i*-C).

2.4. Preparation of $[Li(THF)_2(\mu\text{-}Br)_2Zn\{C(SiMe_3)_2(SiMe_2NPhMe)\}]$ *(4)*

A solution of LiMe (2.5 cm^3, 4.0 mmol) in diethyl ether was added slowly to a stirred solution of **6** (1.15 g, 3.56 mmol) in THF (40 cm^3) at room temperature. The mixture was stirred overnight, then added to a stirred solution of $ZnBr_2$ (0.80 g, 3.56 mmol) in THF (15 cm^3) at −90 °C. This mixture was then allowed to warm slowly to room temperature and solvents removed to leave an orange solid, which was extracted with hexane (2 × 20 cm^3). The volume of the combined extract was reduced to 5 cm^3 and the solution was kept at −30 °C for 2 days to give colourless crystals of **4** (1.84 g. 74%), m.p. 245–249 °C. Anal. Calc. for $C_{24}H_{48}Br_2LiNO_2Si_3Zn$: C, 41.26; H, 6.87; N, 2.00. Found: C, 41.09; H, 6.93; N, 1.92%. ^1H NMR (C_6D_6): δ 0.55 (18H, s, $SiMe_3$), 0.73 (6H, s, $SiMe_2$), 1.30 (8H, m, THF), 2.86 (3H, s, NMe), 3.49 (8H,

Table 1
Crystal data for compounds **2a** and **4**

	2a	**4**
Chemical formula	$C_{22}H_{60}Br_2N_2Si_6Zn_2$	$C_{24}H_{48}Br_2LiNO_2Si_3Zn$
Formula weight	811.8	699.03
T (K)	173(2)	173(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a (Å)	9.1945(2)	13.6053(1)
b (Å)	9.2103(2)	8.9953(1)
c (Å)	13.5042(4)	29.0818(3)
α (°)	75.060(1)	87.306(1)
β (°)	77.882(1)	84.259(1)
γ (°)	60.704(1)	69.225(1)
U (Å^3)	958.84(4)	3310.8(1)
Z	1	4
μ (mm^{-1})	3.54	3.28
$R_1 wR_2 I > 2\sigma(I)$	0.033, 0.083	0.070, 0.180
All data	0.038, 0.087	0.085, 0.194
Measured/independent reflections/$R_{(\text{int})}$	8575/3420/0.039	36761/12056/0.052
Reflections with $I > 2\sigma(I)$	3098	9824

m, THF), 7.15 (1H, m, *p*-H), 7.24 (2H, m, *m*-H), 7.43 (2H, dd, *o*-H). ^{13}C NMR: δ 6.3 ($SiMe_3$), 7.2 ($SiMe_2$), 11.1 (CSi_3), 25.3 (THF), 35.0 (NMe), 68.5 (THF), 114.4 (*o*-C), 117.1 (*p*-C), 131.6 (*m*-C), 152.6 (*i*-C). ^{29}Si NMR: $\delta - 4.0$ ($SiMe_3$), 6.3 ($SiMe_2$). ^{7}Li NMR: δ 0.05. No change was observed in the ^{1}H NMR spectrum when **4** was heated in either hexane or THF for 2 h.

2.5. Crystallography

Data for **2a** and **4** were collected on a Kappa CCD diffractometer and full matrix least squares refinement was by use of SHELX-97 programs. In **4**, the asymmetric unit contains two independent molecules. One is well-defined. The other has an alternative lower occupancy (0.17) set of positions for one of the bridging bromides and nearly all the atoms of the alkyl group. In the disordered molecule the lower occupancy sites were left isotropic and in both positions the phenyl group was assumed to be a rigid body. The value of U_{iso} for the lower occupancy position of C11 was fixed. Further details are given in Table 1.

3. Results and discussion

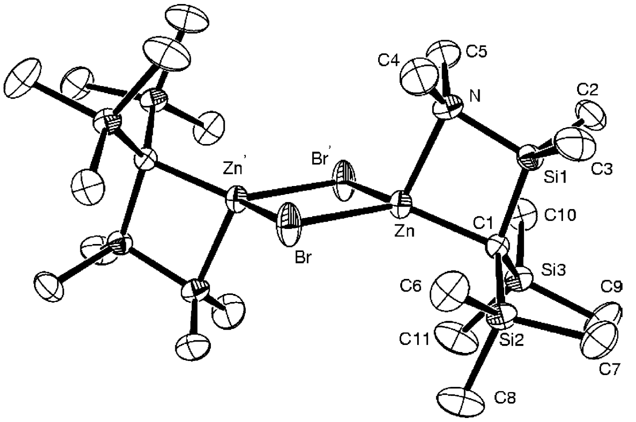

Fig. 1. The molecular structure of $[\overline{\text{ZnBrC(SiMe}_3)_2(\text{SiMe}_2\text{N}}\text{Me}_2)]_2$ **(2a)** with 50% thermal ellipsoids.

The zinc compound **2a** was made without difficulty from the lithium reagent **3**. The new ligand precursor $(Me_3Si)_2\{(PhMeN)Me_2Si\}CH$ (**6**) was made from $(Me_3Si)_2(Me_2BrSi)CH$ and two equivalents of *N*-methylaniline. It was purified by distillation and fully characterised by chemical analysis and NMR spectroscopy. The low values of $^1J_{CH}$ (97 Hz) and $^1J_{SiC}$ (37–43 Hz) are characteristic of compounds containing the Si_3CH core [14]. The reaction between **6** and methyllithium at room temperature gave a mixture of unchanged **6** and what appeared to be the lithium compound $Li(THF)_2\{C(SiMe_3)_2(SiMe_2NPhMe)\}$ (**7**). With a longer reaction time the proportion of **7** decreased, suggesting that it was being removed by an as yet unidentified side reaction. Attempts to obtain crystals of **7** suitable for an X-ray structure determination were not successful, but its formation was confirmed by the isolation in reasonable yield and characterisation of the lithium zincate **4**, after treatment of the mixture obtained from $(Me_3Si)_2\{(PhMeN)Me_2Si\}CH$ (1 mol) and LiMe (1 mol) with zinc bromide (1 mol).

The bromide **2a** is isomorphous with the previously described cobalt compound **2b**. The dimeric molecules, shown in Fig. 1, lie on a centre of symmetry so that the

Table 2
Selected bond lengths (Å) and angles (°) in $[\overline{\text{ZnBrC(SiMe}_3)_2(\text{SiMe}_2\text{N}}\text{Me}_2)]_2$ **(2a)** and $[Li(THF)_2(\mu\text{-}Br)_2Zn\{C(SiMe_3)_2(SiMe_2NPhMe)\}]$ **(4)**

	2a[a]	**4**[b,c]
Zn–C	2.045(3)	2.014(5)
Zn–N	2.152(2)	
Zn–Br or Br1	2.4614(4)	2.4028(9)
Zn–Br′ or Br2	2.4963(4)	2.4406(9)
Si–C[d]	1.868(3)	1.875(6)
Si–Me[d]	1.875(4)	1.876(8)
Br–Zn–Br′ or Br1–Zn–Br2	93.577(14)	100.77(3)
Zn–Br–Zn	86.423(14)	
Br–Zn–C1	131.09(8), 127.06(8)	131.04(15), 125.27(15)

[a] Br–Zn–N 110.03(7)°, 106.42(7)°; N–Zn–C 85.70(10)°.

[b] For the undisordered molecule, values for the disordered molecules do not differ significantly.

[c] Br1–Li–Br2 94.9(4)°; Li–Br1–Zn 81.6(3)°; Li–Br2–Zn 80.6(3)°.

[d] Average values, with e.s.d.'s of individual measurements in parentheses.

Zn_2Br_2 ring is planar. As the Zn–Br and Zn–Br′ bond lengths are significantly different, the dimer is not disposed quite symmetrically about the C_2N_2 plane perpendicular to that of the central ring. Bond lengths and angles are given in Table 2. The Zn–C bond lengths in **2a** and in the pyridyl derivative **1** [2.037(4) Å] are not significantly different, but the Zn–N bond in **2a** [2.152(2) Å] is longer than that in **1** [Zn–N 2.077(4) Å], reflecting the weaker basicity of the dimethylamido nitrogen and possibly greater strain in a four-membered than in a five-membered ring. The coordination at zinc is that of an extremely distorted tetrahedron with the Br_2ZnC system nearly planar (sum of angles at Zn 352°). The central ring may be compared with that in the anion $Zn_2Br_6^{2-}$, in which the Zn–Br bond length is 2.501(3) Å but the Br–Zn–Br angles (108–112°) are close to the tetrahedral value [15]. It is noteworthy that although the length of the Zn–C bond in **2a** is similar to that of the Co–C bond [2.065(8) Å] in **2b**, the Zn–N bond is significantly longer than the Co–N bond [2.087(7) Å], showing that zinc(II) is a weaker Lewis acid than cobalt(II) towards the NMe_2 ligand.

The mass spectrum of **2a** showed several weak peaks having patterns corresponding to the Zn_2Br_2 fragment, indicating that the species observed in the crystal is preserved in the gas phase.

The structure of the lithium alkyldibromozincate **4** is shown in Fig. 2. The $LiBr_2Zn$ ring is folded with an angle of 17° along the Br···Br vector, with the Zn pulled towards the organosilicon fragment bearing the NMePh group. However, the Zn···N distance (3.76 Å) is considerably greater than those in **1** or **2a**, indicating that the *N*-methylanilido group is too weakly basic to coordinate to the metal centre. The zinc is only three-coordinate, as in $[(PhMe_2Si)_3CZnCl)]_2$ [4], and the bonds to bromine and carbon are almost coplanar (sum of angles at Zn 357°). The structure may be compared with that of the magnesate **8**, in which there is an additional molecule of THF attached to the metal centre [16]. The THF is absent in **4**, probably because the NMePh group is larger than Me and zinc is both smaller and less acidic than magnesium. The weakening of the Zn–N bond is associated with a strengthening of the bridging Zn–Br bonds, which are shorter to the three-coordinate zinc in **4** [2.4028(9) and 2.4406(9) Å] than those to the four-coordinate zinc in **1** [Zn–Br 2.4601(6) and 2.5398(7) Å] or **2a** [2.4614(4) and 2.4963(4) Å]. The angles within the MBr_2Zn rings (M = Li or Zn) in **2a** and **4** (Table 2) reflect transannular inner shell repulsions, e.g. the Br–Zn–Br angle is narrower and the M–Br–Zn angle is wider when M is Zn. Although no other structure containing a $LiBr_2Zn$ ring appears to be available for comparison, three-coordinate zinc has been found in a number of compounds containing bulky ligands [17].

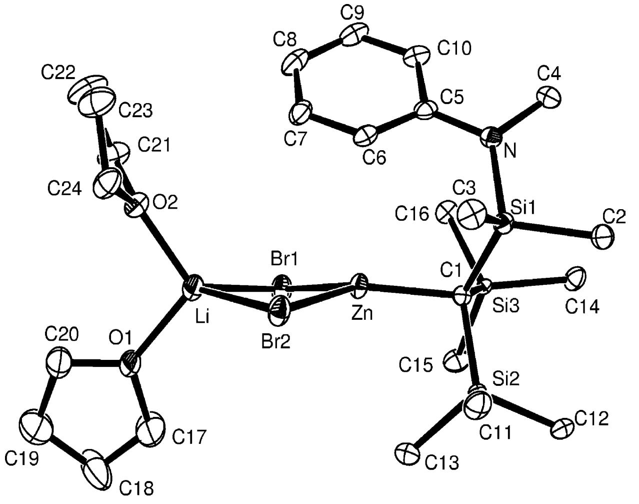

Fig. 2. The structure of the ordered molecule of **4** with 20% thermal ellipsoids.

We reported previously that the lithium organocadmates $Li(THF)CdX_2C(SiMe_3)_3$ (X = Cl or Br), obtained from the reaction between $LiC(SiMe_3)_3$ and the halides CdX_2, decomposed on heating to give lithium halides and organocadmiun halides [16]. No similar reaction was detected when the zincate **4** was heated under reflux in either hexane or THF. No lithium halide was precipitated and no change was detected in the NMR spectrum.

Although we have not yet examined the potential of **2a** and **4** as ring opening polymerisation catalysts, their isolation and characterisation suggest that by making compounds of this type with a series of substituents at nitrogen it may be possible to build derivatives having a range of sterically constrained zinc coordination sites at which transformations or polymerisations of small molecules may be envisaged.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC nos. 228791 and 228792 for compounds **2a** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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