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New Organo- and Aminozinc Derivatives of Primary Amines

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5 Five new zinc derivatives of primary amines [R'ZnN(H)R]$_2$ [R = SiPh$_3$, R' = Me (**1**), N(SiMe$_3$)$_2$ (**4**); R = Si(NMe$_2$)$_3$, R' = Me (**2**), Et (**3**), N(SiMe$_3$)$_2$ (**5**)] have been synthesised by reaction of R'$_2$Zn and H$_2$NR. All five species are dimers in which the N-H groups are disposed in a *trans* manner about a central Zn$_2$N$_2$ ring. In **1** and **4** the coordination at zinc is trigonal planar, while in **2**, **3**, **5** the zinc is in a distorted tetrahedral environment due to additional Me$_2$N:→Zn coordination from one SiNMe$_2$ group. **5** was found
10 to be generally resistant to NH deprotonation by bases such as MN(SiMe$_3$)$_2$ (M = Li, K) or Zn[N(SiMe$_3$)$_2$]$_2$, but reacts with Sn[N(SiMe$_3$)$_2$]$_2$ to give the tin-free, tetrameric mixed zinc-imido/amido species,[{(Me$_3$Si)$_2$N}{(Me$_2$N)$_3$SiN(H)}{(Me$_2$N)$_3$SiN}Zn$_2$]$_2$ (**6**) which can be viewed as part of a hexameric Zn$_6$N$_6$ drum which has lost a Zn$_2$N$_2$ ring.

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Introduction

15 The first zinc amide, Zn(NEt$_2$)$_2$, was synthesised by Frankland in 1856,[1] since when the reaction of zinc complexes with secondary amines has been systematically investigated in great detail.[2] In comparison, studies into the reaction of organozinc
20 reagents with primary amines are far less extensive.[3] The direct reaction of several primary amines RNH$_2$ (R = ^{t}Bu,[3a] Ph,[3a] Mes,[3a] napthyl,[3b] adamantyl,[3c] ^{i}Pr$_3$Si[3c,4]) with R$_2$Zn (most commonly, but not exclusively,[3a,4] the commercially available reagents ZnMe$_2$ and ZnEt$_2$) with the subsequent elimination of alkane have been
25 explored, resulting in either monomeric, dimeric or trimeric variants on [R'ZnN(H)R]$_n$ determined by the steric demand of the substituents bonded to the zinc and nitrogen atoms. In none of these examples has the further deprotonation of the amide and subsequent formation of zinc imido complexes been observed,
30 even under forcing conditions. Interestingly, within similar zincated primary phosphane and arsane complexes, [R'ZnE(H)R]$_2$ (E = P, As), the increased acidic nature of the E-H bond results in the self-condensation of the complex and subsequent formation of bridging phosphanediide and arsanediide species.[4-5]

35 Interest in this general area is now driven by the continued requirement for volatile zinc compounds for use in chemical vapour deposition (CVD) processes, where the presence of N-H bonds in the precursor may aid the decomposition process.[3d] Furthermore, in addition to acting as precursor for the deposition
40 of widely exploited n-type ZnO,[6] systems with a high nitrogen content may lead to nitrogen doping and a switch to p-type behaviour or, conceivably, deposition of the nitride Zn$_3$N$_2$. Indeed, oxidation of Zn$_3$N$_2$ has been reported as a viable route to p-type ZnO by N-doping.[7] In this paper we report the synthesis
45 and characterisation of further examples of R'ZnN(H)R [R' = Me,

R = SiPh$_3$, Si(NMe$_2$)$_3$; R' = Et, R = Si(NMe$_2$)$_3$], the novel species (Me$_3$Si)$_2$NZnN(H)R [R = SiPh$_3$, Si(NMe$_2$)$_3$], along with our attempts to elaborate these species further by reaction of the residual N-H unit, leading to the formation of the unprecedented
50 imido-containing teteramic species Zn$_4$[N(SiMe$_3$)$_2$]$_2$[N-Si(NMe$_2$)$_3$]$_2$[N(H)Si(NMe$_2$)$_3$]$_2$ (**6**).

Experimental

General Information:

All operations were performed under an atmosphere of dry
55 argon using standard Schlenk line and glovebox techniques. Hexanes and toluene solvents were dried using a commercially available solvent purification system (Innovative Technology Inc.) and degassed under argon prior to use. Deuterated benzene (C$_6$D$_6$) Toluene (d$_8$-Toluene) and THF (d$_8$-THF) NMR solvents
60 were purchased from Fluorochem and dried over potassium before isolating *via* vacuum distillation. All dry solvents were stored under argon in Young's ampoules over 4 Å molecular sieves. 2 M Dimethylzinc (ZnMe$_2$) and 1 M diethylzinc (ZnEt$_2$) solutions were prepared accordingly from the neat reagent,
65 supplied by SAFC HiTech. [Ph$_3$SiNH$_2$],[8] [(Me$_2$N)$_3$SiNH$_2$],[9] [Zn{N(SiMe$_3$)$_2$}$_2$],[10] and [Sn{N(SiMe$_3$)$_2$}$_2$][11] were prepared according to published procedures.

All solution state ^{1}H and ^{13}C{^{1}H} NMR spectra obtained at ambient temperature (25 ^{o}C) were recorded with a Bruker Avance
70 300 spectrometer, whilst ^{29}Si NMR spectra were recorded using a Bruker Avance 500 spectrometer. VT-NMR experiments were performed in d$_8$-Toluene using a Bruker Avance 400 spectometer. ^{1}H and ^{13}C NMR chemical shifts are given in ppm and referenced internally to residual non-deuterated solvent resonances.[12] The
75 following abbreviations are used: s (singlet), t (triplet), q (quartet), m (multiplet) and br (broad). Elemental analyses were

performed externally by London Metropolitan University Elemental Analysis Service, UK.

Synthesis of [{MeZnN(H)SiPh₃}₂] (1): Ph₃SiNH₂ (1.38 g, 5 mmol) was dissolved in hexanes (20 mL), then treated with a 2 M toluene solution of ZnMe₂ (2.5 mL, 5 mmol). The reaction solution was stirred at ambient temperature for 24 h, forming a white precipitate. Volatiles were then removed *in vacuo*. Slow recrystallization of the residue from hexanes at ambient temperature gave the product as colourless crystals. Yield: 1.05 g, 59%. $C_{19}H_{19}NSiZn$ (354.83): calcd C 64.34, H 5.36, N 3.95; found C 64.74, H 5.38, N 3.95. ^1H NMR (300 MHz, C_6D_6): δ_H = 7.74 – 7.63 (br m, 6 H, C_6H_5), 7.34 – 7.16 (br m, 9 H, C_6H_5), 0.01 (s, 1 H, N*H*), -0.31 (s, 3 H, Zn*CH₃*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ_C = 138.5, 138.1, 130.5, 126.1 (C_6H_5), -9.2 (Zn*CH₃*). ^{29}Si (99.35 MHz, C_6D_6): δ_{Si} = -11.9.

Synthesis of [{MeZnN(H)Si(NMe₂)₃}₂] (2): A solution of (Me₂N)₃SiNH₂ (0.88 g, 5 mmol) in hexanes (10 mL) was treated with a 2 M toluene solution of ZnMe₂ (2.5 mL, 5 mmol). The reaction solution was stirred at ambient temperature for 24 h and then volatiles were removed *in vacuo*. Crystallisation of the residue from hexanes at -28 °C gave the product as colourless crystals. Yield: 0.78 g, 61%. $C_7H_{22}N_4SiZn$ (255.74): calcd C 32.89, H 8.61, N 21.93; found C 32.76, H 8.48, N 21.26. ^1H NMR (300 MHz, C_6D_6): δ_H = 2.45 (s, 18 H, NC*H₃*), 0.16 (s, 1 H, N*H*), -0.25 (s, 3 H, Zn*CH₃*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ_C = 38.6 (N*CH₃*), -12.6 (Zn*CH₃*). ^{29}Si (99.35 MHz): δ_{Si} = -28.7.

Synthesis of [{EtZnN(H)Si(NMe₂)₃}₂] (3): A solution of (Me₂N)₃SiNH₂ (0.35 g, 2 mmol) in hexanes (10 mL) was slowly treated with a 1 M solution of ZnEt₂ (2 mL, 2 mmol) in hexanes. The reaction was stirred at ambient temperature for 24 h and volatiles were then removed *in vacuo*. Crystallisation of the residue from toluene at -28 °C gave the product as colourless crystals. Yield: 0.20 g, 37%. $C_8H_{24}N_4SiZn$ (269.77): calcd C 35.62, H 8.97, N 20.77; found C 35.51, H 9.13, N 20.66. ^1H NMR (300 MHz, C_6D_6): δ_H = 2.48 (s, 18 H, NC*H₃*), 1.60 (t, 3 H, ZnCH₂C*H₃*, $^3J_{CH2CH3}$ = 8.1 Hz), 0.64 (q, 2 H, ZnC*H₂*CH₃, $^3J_{CH2CH3}$ = 8.1 Hz), 0.16 (s, 1 H, N*H*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ_C = 38.7 (N*CH₃*), 13.0 (ZnCH₂*CH₃*), 1.83 (Zn*CH₂*CH₃) ^{29}Si (99.35 MHz): δ_{Si} = -28.9.

Synthesis of [{(Me₃Si)₂NZnN(H)SiPh₃}₂] (4): Ph₃SiNH₂ (0.55 g, 2 mmol) was dissolved in hexanes (10 mL), then treated with a solution of Zn[N(SiMe₃)₂]₂ (0.77 g, 2 mmol) in hexanes (10 mL). The reaction solution was stirred at ambient temperature for 24 h, forming a white precipitate. Volatiles were then removed *in vacuo*. Recrystallization of the residue from toluene at -28 °C gave the product as colourless crystals. Yield: 0.31 g, 31%. $C_{24}H_{34}N_2Si_3Zn$ (500.18): calcd C 57.63, H 6.85, N 5.60; found C 57.77, H 6.67, N 5.45. ^1H NMR (300 MHz, d_8-THF): δ_H = 7.66 – 7.02 (br m, 15 H, C_6H_5), 0.13 – 0.05 (m, 13 H, SiC*H₃*), -0.03 – -0.18 (br m, 3 H, SiC*H₃*), -0.19 – -0.36 (br s, 2 H, SiC*H₃*). $^{13}C\{^1H\}$ NMR (75.5 MHz, d_8-THF): δ_C = 140.3, 136.6, 136.3, 129.9, 129.5, 128.4, 128.3 (C_6H_5), 5.7 (Si*CH₃*). ^{29}Si (99.35 MHz, d_8-THF): δ_{Si} = -5.0 (*Si*Me₃), -16.1 (*Si*Ph₃).

Synthesis of [{(Me₃Si)₂NZnN(H)Si(NMe₂)₃}₂] (5): A solution of (Me₂N)₃SiNH₂ (0.71 g, 4 mmol) in hexanes (6 mL) was treated with a solution of Zn[N(SiMe₃)₂]₂ (1.54 g, 4 mmol) in hexanes (6 mL). The reaction solution was stirred at ambient temperature for 24 h, forming a white precipitate. The volume of the reaction solution was partially reduced *in vacuo* and the precipitate re-dissolved with gentle heating. Crystallisation from the reaction solution at 5 °C gave the product as colourless crystals. Yield: 1.07 g, 67%. $C_{12}H_{37}N_5Si_3Zn$ (401.09): calcd C 35.93, H 9.30, N 17.46; found C 35.82, H 9.45, N 17.55. ^1H NMR (300 MHz, C_6D_6): δ_H = 2.55 (s, 6 H, NC*H₃*), 2.50 (s, 12 H, NC*H₃*), 0.25 (s, 3 H, SiC*H₃*), 0.24 (s, 12 H, SiC*H₃*), 0.19 (s, 3 H, SiC*H₃*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ_C = 39.2 (N*CH₃*), 5.6 (Si*CH₃*). ^{29}Si (99.35 MHz, C_6D_6): δ_{Si} = -3.9 (*Si*Me₃), -28.1 (*Si*NMe₂).

Synthesis of [{(Me₃Si)₂N}{(Me₂N)₃SiN(H)}{(Me₂N)₃SiN}Zn₂]₂ (6): A solution of **5** (0.40 g, 0.5 mmol) in hexanes (10 mL) was treated with a solution of Sn[N(SiMe₃)₂]₂ (0.22 g, 0.5 mmol) in hexanes (10 mL). The reaction solution was stirred for 72 h, and volatiles were then removed *in vacuo*. Crystallisation of the residue from hexanes at -28 °C gave the product as small, off-white crystals. Yield: 0.03 g, 9%. ^1H NMR (500 MHz, d_8-toluene): δ_H = 2.94-2.35 (br m, NC*H₃*), 0.65-0.16 (br m, SiC*H₃*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ_C = 39.5, 39.0, 38.7 (N*CH₃*), 6.4, 5.2, 2.6, 1.4 (Si*CH₃*). ^{29}Si (99.35 MHz, C_6D_6): δ_{Si} = 2.4, -0.6 (*Si*Me₃), -20.2, -27.8, -31.1 (*Si*NMe₂).
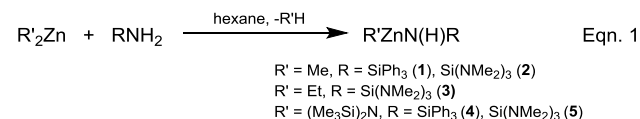
Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo-Kα radiation (λ = 0.71073 Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programmes.[13] Specific details: **1** contains two independent molecules and one molecule of toluene in the asymmetric unit; **4** also contains a molecule of toluene disordered over two positions.

Results and Discussion

Synthesis and Structures

New alkylzinc amido complexes R'Zn(NH)R [R' = Me, R = SiPh₃ (**1**), R' = Me, R = Si(NMe₂)₃ (**2**); R' = Et, R = Si(NMe₂)₃ (**3**)] have been prepared by reaction of RNH₂ and R'₂Zn in hexane. Similarly, (Me₃Si)₂NZnN(H)R [R = SiPh₃ (**4**), Si(NMe₂)₃ (**5**)] have been prepared analogously starting from (Me₃Si)₂Zn (Eqn 1):

$$R'_2Zn\ +\ RNH_2\ \xrightarrow{\text{hexane, -R'H}}\ R'ZnN(H)R \qquad \text{Eqn. 1}$$

R' = Me, R = SiPh₃ (**1**), Si(NMe₂)₃ (**2**)
R' = Et, R = Si(NMe₂)₃ (**3**)
R' = (Me₃Si)₂N, R = SiPh₃ (**4**), Si(NMe₂)₃ (**5**)

Complexes **1–5** are colourless air-sensitive solids, soluble in common organic solvents; yields were in the range 31 – 67%. Despite numerous attempts to substitute the remaining R' group (1:2 reaction stoichiometry, excess amine, reflux, change of solvent to either THF or toluene), only mono-substituted

R'ZnN(H)R species, could be isolated.

The ^{1}H NMR spectra of **1-3** each display the expected resonances attributed to the substituents bonded to the silicon atoms (Ph or NMe$_2$). Additionally the spectra show a single resonance [δ = - 0.31 (**1**), -0.25 (**2**), 0.64 ppm (**3**)] that may be assigned to a methyl or methylene group bonded to the zinc atom, along with a broad singlet [δ = 0.01 (**1**), 0.16 (**2**), 0.16 ppm (**3**)] that may be attributed to the remaining NH proton. Integration of these resonances show the {R$_3$Si}, {ZnMe/Et} and {NH} moieties are present in a 1:1:1 ratio, consistent with the formation of a zinc amide with the empirical formula Me/Et-ZnN(H)SiR$_3$ rather than a zinc imido species. In the case of **2**, the NMe$_2$ groups all appear to be equivalent, despite this not being the case in the solid state (see below). The spectra are more complex for the more sterically encumbered **4** and **5**. The ^{1}H NMR spectrum of **4** has a complex multiplet of signals corresponding to the four Me$_3$Si groups, while the N-H signal is not observed. The ^{13}C NMR has only a singlet for the associated carbon centres. It appears that the hydrogen atoms of these groups become non-equivalent due to restricted rotation in this congested molecule.
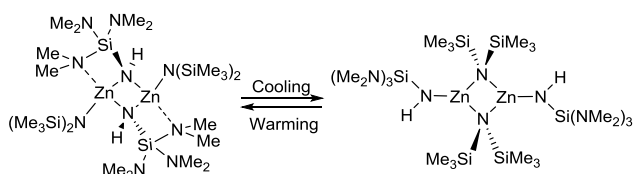
Scheme 1 Proposed species that exist in equilibrium for complex **5**.

At 298 K, the ^{1}H NMR spectra of **5** shows two signals for the NMe$_2$ groups in 2:1 ratio consistent with the solid state structure incorporating the μ-(NMe$_2$)Si(NMe$_2$)$_2$ moiety; there is also some non-equivalence to the Me$_3$Si groups (three signals in 4:1:1 ratio) consistent with hindered rotation of these groups. Again, the N-H resonance is not observed within the ^{1}H NMR sectrum.
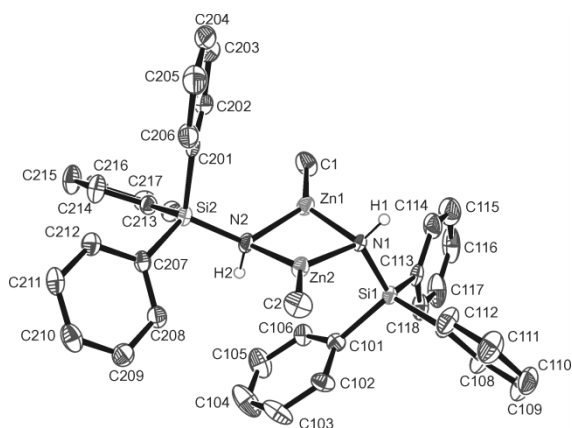

Fig. 1 The structure of **1** showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. C(107) and C(218) are hidden behind C(112) and Si(2), respectively. Only one of two molecules in the asymmetric unit is shown; a co-crystallised molecule of toluene has also been omitted for clarity. Selected geometric data: Zn(1)-N(1) 2.015(4), Zn(1)-N(2) 2.048(4), Zn(2)-N(1) 2.036(4), Zn(2)-N(2) 2.037(4), Si(1)-N(1) 1.733(4), Si(2)-N(2) 1.726 (4) Å; Zn(1)-N(1)-Zn(2) 89.40(15), Zn(1)-N(2)-Zn(2) 88.47(16), N(1)-Zn(1)-N(2) 89.77(16), N(1)-Zn(2)-N(2) 89.48(15), N(1)-Zn(1)-C(1), 136.6(2), N(2)-Zn(1)-C(1) 133.1(2), N(1)-Zn(2)-C(2) 134.5(2), N(2)-Zn(2)-C(2) 136.0(2), Zn(1)-N(1)-Si(1) 115.97(19), Zn(2)-N(1)-Si(1) 112.71(19) °.
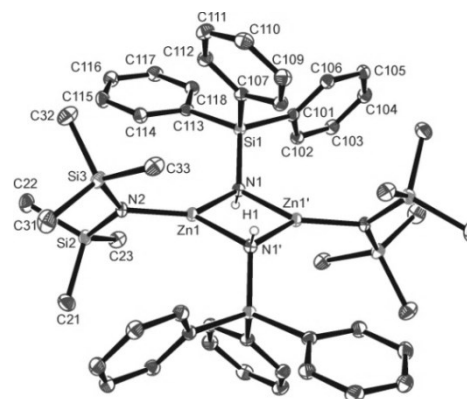

Fig. 2 The structure of **4** showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. A co-crystallised molecule of disordered toluene has also been omitted for clarity Selected geometric data: Zn(1)-N(1) 2.0228(17), Zn(1)-N(1') 2.0371(17), Zn(1)-N(2) 1.8873(16), N(1)-Si(1) 1.7480(18), N(2)-Si(4) 1.7208(17), N(2)-Si(2) 1.7124(18)   Å, N(1)-Zn(1)-N(2) 132.27(7), N(1)-Zn(1)-N(1') 91.79(7), N(2)-Zn(1)-N(1') 135.94(7)' Si(1)-N(1)-Zn(1) 119.30(10), Si(1)-N(1)-Zn(1') 119.18(10), Zn(1)-N(1)-Zn(1') 88.21(7) °. Symmetry operation: 1-x,1-y,1-z.

However, on cooling a sample of **5** to 218 K, far from resolving these different environments, the ^{1}H spectrum simplifies (singlets at δ ca 2.56, 0.38 ppm) which are contrary to the observed solid-state structure. We have no unambiguous rationale for this observation, but suggest that an alternative structure involving μ$_2$-N(SiMe$_3$)$_2$ and terminal N(H)Si(NMe$_2$)$_3$ groups may exist at low temperature (Scheme 1), as is the case for [^{t}BuZnN(SiMe$_3$)$_2$]$_2$[14] and [C$_6$F$_5$ZnN(SiMe$_3$)$_2$]$_2$.[14]

The structures of **1 - 5** are shown in Figures **1 – 5** and all five species are dimeric in nature. Both **1** (Figure 1) and **4** (Figure 2) adopt structures in which R(H)N groups bridge zinc centres, with the bulky Ph$_3$Si groups disposed in an anti-manner about the central Zn$_2$N$_2$ ring. The structures are analogous to [R'ZnN(H)Si^{i}Pr$_3$]$_2$ (R = Me, Et)[3c] in embodying a three-coordinate, trigonal planar metal centre geometry, with no further coordination by either free amine[3c, 3d] or solvent, which is common for reactions carried out in donor solvents such as THF.[3a, 3b]

Fig. 3 The structure of **2** showing the labelling scheme used in the text; thermal ellipsoids are at the 35% probability level. Selected geometric data: Zn(1)-N(1) 2.1422(14), Zn(1)-N(1') 2.0165(13), Zn(1)-N(2) 2.3377(14), Si(1)-N(1) 1.7023(14), Si(1)-N(2) 1.7769(15), Si(1)-N(3) 1.7056(14), Si(1)-N(4) 1.7131(14) Å; C(1)-Zn(1)-N(1), 131.24(7), C(1)-Zn(1)-N(1') 131.37(7), C(1)-Zn(1)-N(2) 111.19(8), N(1')-Zn(1)-N(2) 103.02(5), N(1)-Zn(1)-N(2) 73.23(5), N(1)-Zn(1)-N(1') 90.65(5), Zn(1')-N(1)-Si(1) 121.21(8), Zn(1)-N(1)-Si(1) 93.82(6), Zn(1)-N(1)-Zn(1') 89.35(5), Zn(1)-N(2)-Si(1) 85.52(5), Zn(1)-N(2)-C(21) 106.73(12), Zn(1)-N(2)-C(22) 112.91(13), Si(1)-N(2)-C(21) 118.57(12), Si(1)-N(2)-C(22) 119.48(12), C(21)-N(2)-C(22) 110.25(14) °. Symmetry operation: 1-x,1-y,-z
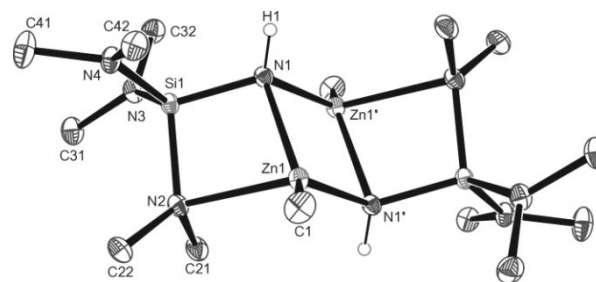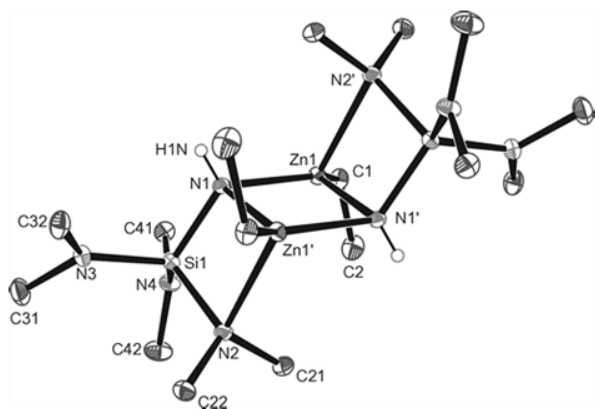
Fig. 4. The structure of **3** showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. Selected geometric data: Zn(1)-N(1) 2.0208(15), Zn(1)-N(1') 2.1327(16), Zn(1)-N(2') 2.3425(15), Si(1)-N(1) 1.7039(16), Si(1)-N(2) 1.7795(15), Si(1)-N(3) 1.7129(16), Si(1)-N(4) 1.7111(17) Å; C(1)-Zn(1)-N(1)131.76(7),C(1)-Zn(1)-N(1') 130.10(7), C(1)-Zn(1)-N(2') 112.40(7), N(1)-Zn(1)-N(1') 90.65(6), N(1)-Zn(1)-N(2') 102.31(6), N(1')1-Zn(1)-N(2') 73.48(6), Si(1)-N(1)-Zn(1) 119.24(9), Si(1)-N(1)-Zn(1') 94.37(7), Zn(1)-N(1)-Zn(1') 89.35(6) °. Symmetry operation: 1-x,-y,-z.

The Zn-N bonds to the bridging nitrogen atoms are typical of those involved in Zn_2N_2 rings reported in the Cambridge Crystallographic Database (1.997 Å - 2.109 Å),[15] and are longer [2.015(4) – 2.0371(17) Å] than the exocyclic Zn-N bond in **4** [1.8873(16) Å].In contrast, **2** (Figure 3), **3** (Figure 4) and **5** (Figure 5), each of which incorporate the $N(H)Si(NMe_2)_3$ ligand, are dimeric but embody four-coordinated zinc atoms by virtue of both μ_2-N(H)R and μ_2-NMe$_2$ moieties; the bulky $Si(NMe_2)_3$ groups are, as in **1**, **2**, in an *anti*-arrangement with respect to the central Zn_2N_2 ring.

There is a clear asymmetry in the distinct Zn-N bonds within the central Zn_2N_2 ring [2.0165(13) – 2.0397(15) *vs* 2.1035(15) – 2.1422(14) Å], along with a longer Zn-N bond within the ZnN_2Si ring [2.3377(14) – 2.4282(16) Å]. The Si-N bond associated with the μ_2-NMe$_2$ group is, not surprisingly, longer [1.7769(15) – 1.7854(17) Å] than the remaining Si-N bonds [1.7023(14) – 1.7225(15) Å], and, while the exocyclic Zn-N bond in **5** is still the shortest in this trio of structures [1.9264(14) Å] it is marked longer than the same bond to three-coordinate zinc in **4**. The tetrahedral geometry about zinc is severely distorted to accommodate the two fused Zn_2N_2 and ZnN_2Si rings.

In attempts to react the remaining N-H bond in these species to form bimetallic species, **5**, as representative, was treated with excess $M[N(SiMe_3)_2]$ (M = Li, K) or $Zn[N(SiMe_3)_2]_2$, but only starting materials could be isolated from these reactions. Remarkably, however, the stoichiometric reaction of **5** with $Sn[N(SiMe_3)_2]_2$ afforded the mixed amino-imido tetramer $Zn_4[N(SiMe_3)_2]_2[NSi(NMe_2)_3]_2[N(H)Si(NMe_2)_3]_2$ (**6**) albeit in very low yield (9%). It is unclear why the tin silylamide deprotonates **5** where other bases fail, nor have we ascertained the fate of the tin in this reaction. Compound **6** is, as far as we are aware, only the second example of an imido-zinc complex, and the first to be prepared from a primary amine as reagent; the only other example of a bis-zinc imido complex, bis-(ethylzinc)imido-1,2-di(2-pyridyl)ethane, was prepared from the secondary bis-(2-pyridylmethyl)amine *via* a C-C bond forming process.[16] Furthermore, the formulation of **6** only has tenuous precedent in that of $Zn_4Et_2(NHR)_4(OEt)_2$ (R = 2,6-^{i}Pr$_2$C$_6$H$_3$).[3a]

The structure of **6** (Figure 6) is made up of three Zn_2N_2 rings with two common edges, with the outer rings symmetry related by virtue of a two-fold axis running vertically down through the centre of the middle Zn_2N_2 ring.
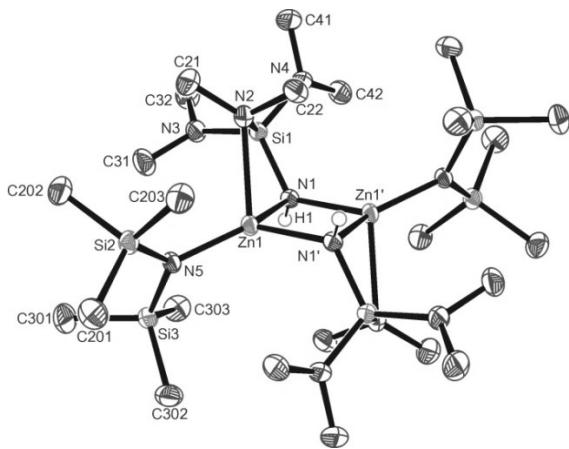

Fig. 5. The structure of **5** showing the labelling scheme used in the text; thermal ellipsoids are at the 40% probability level. Selected geometric data: Zn(1)-N(1) 2.1035(15), Zn(1)-N(2) 2.4282(16), Zn(1)-N(1') 2.0397(15), Zn(1)-N(5) 1.9264(14), Si(1)-N(1) 1.7225(15), Si(1)-N(2) 1.7854(17), Si(1)-N(3) 1.7135(17), Si(1)-N(4) 1.7079(16), Si(10)-N(5) 1.7195(16), Si(20)-N(5) 1.7152(15) Å; N(1)-Zn(1)-N(2) 71.83(6), N(1)-Zn(1)-N(1') 91.58(6), N(1)-Zn(1)-N(5) 130.59(6), N(1')-Zn(1)-N(2) 104.26(6), N(1')'-Zn(1)-N(5) 130.28(6), N(2)-Zn(1)-N(5) 112.50(6), Si(1)-N(1)-Zn(1) 96.65(7), Si(1)-N(1)-Zn(1') 123.71(9), Zn(1)-N(1)-Zn(1') 88.42(6), C(21)-N(2)-Zn(1) 121.83(13), C(21)-N(2)-Zn(1) 121.83(13), C(21)-N(2)-C(22) 108.89(16), C(22)-N(2)-Zn(1) 106.01(12), C(22)-N(2)-Si(1) 115.37(13), Si(1)-N(2)-Zn(1) 84.35(6), Si(10)-N(5)-Zn(1) 121.87(8), Si(10)-N(5)-Si(20) 120.69(9), Si(20)-N(5)-Zn(1) 117.01(8) °. Symmetry operation: 1-x,-y,1-z.

Fig. 6. The structure of **6** showing the labelling scheme used in the text; thermal ellipsoids are at the 30% probability level. Selected geometric data: Zn(1)-N(1) 2.0487(19), Zn(1)-N(1') 2.0979(19), Zn(1)-N(5) 2.0164(19), Zn(1)-N(2') 2.141(2), Zn(2)-N(1) 1.9382(19), Zn(2)-N(5) 2.1121(19), Zn(2)-N(9) 1.917(2), N(1)-Si(1) 1.681(2), N(5)-Si(2) 1.731(2) Å; N(1)-Zn(1)-N(1') 98.00(7), N(1)-Zn(1)-N(2') 123.71(8), N(1)-Zn(1)-N(5) 92.60(8), N(1')-Zn(1)-N(2') 80.10(8), N(1')-Zn(1)-N(5) 131.74(8), N(2')-Zn(1)-N(5) 130.20(8), N(1)-Zn(2)-N(5) 92.94(8), N(1)-Zn(2)-N(9) 140.39(9), N(5)-Zn(2)-N(9) 125.90(8), Si(1)-N(1)-Zn(1) 139.27(12), Si(1)-N(1)-Zn(1') 91.63(9), Si(1)-N(1)-Zn(2) 126.45(11), Zn(1)-N(1)-Zn(2) 89.11(8), Zn(1)-N(1)-Zn(1') 81.20(7), Zn(1')-N(1)-Zn(3) 123.96(9), Si(2)-N(5)-Zn(1) 125.12(11), Si(2)-N(5)-Zn(2) 121.04(11), Zn(1)-N(5)-Zn(2) 85.31(7) °. Symmetry operation: 1-x,y,1/2-z.

The outer two rings are thus *syn* with respect to the central ring, so overall the structure can be viewed as a fragment of Zn_6N_6 hexagonal drum with one Zn_2N_2 face missing. This is in contrast to the three fused rings in $Zn_4Et_2(NHR)_4(OEt)_2$ (R = 2,6-

5 $^iPr_2C_6H_3$)[3a] in which the two ZnOZnN rings are *anti* with respect to the central Zn_2O_2 ring, generating a staircase structure. There are two distinct zinc centres in **6**, namely trigonal planar three-coordinate Zn(2) and four-coordinated Zn(1) which has a distorted tetrahedral array of ligands. The imido nitrogen has a

10 μ_3-Zn_3 bonding mode with one short [Zn(2)-N(1) 1.9382(19) Å] and two longer [Zn(1)-N(1) 2.0487(19), Zn(1')-N(1) 2.0979(19) Å] bonds to zinc. The μ_2-N(H)R group [N(5)] forms two bonds to zinc of similar strength and comparable to those formed by μ_3-N(1) [2.0164(19), 2.1121(19) Å], while the longest and shortest

15 Zn-N bonds are formed by the μ_2-NMe_2 group [Zn(1')-N(2) 2.141(2) Å] and the terminal $N(SiMe_3)_2$ group [Zn(2)-N(9) 1.917(2) Å], respectively. There are distinct Si-N bonds, ranging from the shortest involving the imido nitrogen [N(1)-Si(1) 1.681(2) Å] to the longest based on bridging N(2) [N(2)-Si-Si(1)

20 1.843(2) A] and spanning the remaining, more typical Si-N bond lengths [1.708(3) – 1.731(2) Å]. The terminal $N(SiMe_3)_2$ groups are bonded to Zn(2) at the outer edges of the array, while the two remaining N-H groups [N(5)-H(5)] are too crowed to participate in any hydrogen bonding. Indeed, the crowding of these two

25 functionalities is probably the reason why formation of the hexameric drum structure, typified by $(^iPrNAlH)_6$[17] or $[PhNMg(THF)]_6$,[18] is incomplete.

The NMR data for **6** reflect the asymmetry in the species. The ^1H NMR signals for both the Me_3Si and Me_2N environments are

30 broad and featureless, which reflects both the extent of non-equivalent environments and possible fluxionality. Similarly, the ^{13}C NMR has 4 signals for the Me_3Si carbons and signals for two non-equivalent Me_3Si environments in the ^{29}Si NMR, while the complexity of the $SiNMe_2$ environments is reflected in four ^{13}C

35 and three ^{29}Si NMR resonances. Additional peaks in the spectra can be attributed to residual **5** in the reaction mixture, whch could not be completely removed from samples of **6,** a feature which is reflected in the poor elemental analysis of **6**: attempts to separate peaks for **5** and **6** using DOSY NMR experements proved

40 unsuccessful.

Conclusions

The synthesis of zinc (amido) complexes have been accomplished through protonolysis of either dialkyl-zinc or diamino-zinc

45 starting materials with primary silyl-amide proligands. Despite successive attemts to force these complexes to undergo a double deprotination of the amide proligand, zinc-imido species where not formed. In attempts to react the remaining N-H bond in these species to form bimetallic species, complex **5**, was treated the

50 metal amides $M[N(SiMe_3)_2]$ (M = Li, K) or exess $Zn[N(SiMe_3)_2]_2$, but only starting materials could be isolated from these reactions. Remarkably, reaction of **5** with $Sn[N(SiMe_3)_2]_2$ affords the unprecidented mixed amino-imido tetramer species $Zn_4[N(SiMe_3)_2]_2[N-$

55 $Si(NMe_2)_3]_2[N(H)Si(NMe_2)_3]_2$ (**6**), albeit in very low yield (9%), in which the imido ligand has a μ_2-bridging role and κ^2-*N,NMe_2* chelating coordination role. To the best of our knowledge, complex **6** repersents the first zinc-imido species formed from a primary amine to have been identified and structurally

60 characterised. While the precise nature of the reaction to form **6** is not understood, attempts to both rationalise this reaction and to produce other zinc imido species are underway.

Table 1 Crystal refinement data for **1-6**

Compound reference	1	2	3	4	5	6
Chemical formula	$C_{83}H_{84}N_4Si_4Zn_4$	$C_{14}H_{44}N_8Si_2Zn_2$	$C_{16}H_{48}N_8Si_2Zn_2$	$C_{62}H_{84}N_4Si_6Zn_2$	$C_{24}H_{74}N_{10}Si_6Zn_2$	$C_{36}H_{110}N_{18}Si_8Zn_4$
Formula Mass	1511.38	511.49	539.54	1184.61	802.21	1281.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
a/Å	26.2840(3)	7.83400(10)	7.9730(2)	11.4310(4)	9.05200(10)	23.8580(4)
b/Å	9.4770(2)	10.0490(2)	18.1740(4)	11.9430(5)	21.7480(3)	18.2210(4)
c/Å	32.3190(4)	15.9980(3)	9.3130(2)	12.9460(5)	10.9160(2)	15.5450(3)
α/°	90.00	90.00	90.00	87.265(2)	90.00	90.00
β/°	110.2770(10)	91.4860(10)	98.8530(10)	71.794(2)	101.0760(10)	100.7600(10)
γ/°	90.00	90.00	90.00	73.697(2)	90.00	90.00
Unit cell volume/Å³	7551.5(2)	1259.00(4)	1333.39(5)	1609.86(11)	2108.93(5)	6638.9(2)
Temperature/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Space group	Cc	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
No. of formula units per unit cell, Z	4	2	2	1	2	4
Absorption coefficient, μ/mm^{-1}	1.365	2.015	1.907	0.896	1.337	1.612
No. of reflections measured	37195	26752	24560	29835	26367	52385
No. of independent reflections	15356	2892	3061	6615	4834	7541
R_{int}	0.0594	0.0569	0.0577	0.0549	0.0430	0.0599
Final R_1 values ($I > 2\sigma(I)$)	0.0489	0.0258	0.0273	0.0346	0.0308	0.0346
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1097	0.0666	0.0613	0.0786	0.0737	0.0758
Final R_1 values (all data)	0.0731	0.0375	0.0393	0.0498	0.0397	0.0603
Final $wR(F^2)$ values (all data)	0.1294	0.0732	0.0668	0.0853	0.0775	0.0848
Goodness of fit on F^2	1.014	1.055	1.093	1.047	1.077	1.040
CCDC number	960127	960128	960131	960129	960130	960132

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