Citation for published version:

Cosham, SD, Hill, MS, Johnson, AL & Molloy, KC 2014, 'New organo- and amidozinc derivatives of primary amines', *Dalton Transactions*, vol. 43, no. 2, pp. 859-864. <https://doi.org/10.1039/c3dt52602j>

DOI:

[10.1039/c3dt52602j](https://doi.org/10.1039/c3dt52602j)

Publication date:

2014

Document Version

Early version, also known as pre-print

[Link to publication](#)

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

New Organo- and Amino zinc Derivatives of Primary Amines

Samuel D. Cosham,^a Michael S. Hill,^a Andrew L. Johnson^a * and Kieran C. Molloy^a

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

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'_2Zn and H_2NR . All five species are dimers in which the N-H groups are disposed in a *trans* manner about a central Zn_2N_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 $Me_2N: \rightarrow Zn$ coordination from one $SiNMe_2$ group. **5** was found 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, $\{(Me_3Si)_2N\} \{(Me_2N)_3SiN(H)\} \{(Me_2N)_3SiN\} Zn_2\}_2$ (**6**) which can be viewed as part of a hexameric Zn_6N_6 drum which has lost a Zn_2N_2 ring.

Introduction

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 reagents with primary amines are far less extensive.³ The direct reaction of several primary amines RNH_2 ($R = ^iBu$,^{3a} Ph ,^{3a} Mes ,^{3a} $naphthyl$,^{3b} $adamantyl$,^{3c} iPr_3Si ^{3c,4}) with R_2Zn (most commonly, but not exclusively,^{3a,4} the commercially available reagents $ZnMe_2$ and $ZnEt_2$) with the subsequent elimination of alkane have been 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, even under forcing conditions. Interestingly, within similar zincated primary phosphane and arsane complexes, $[R'E(H)R]_2$ ($E = P, As$), 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

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 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_3N_2 . Indeed, oxidation of Zn_3N_2 has been reported as a viable route to p-type ZnO by N-doping.⁷ In this paper we report the synthesis 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 $(Me_3Si)_2NZN(H)R$ [$R = SiPh_3$, $Si(NMe_2)_3$], along with our attempts to elaborate these species further by reaction of the residual N-H unit, leading to the formation of the unprecedented imido-containing tetrameric 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 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_6D_6) Toluene (d_8 -Toluene) and THF (d_8 -THF) NMR solvents 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, supplied by SAFC HiTech. $[Ph_3SiNH_2]$,⁸ $[(Me_2N)_3SiNH_2]$,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 1H and $^{13}C\{^1H\}$ NMR spectra obtained at ambient temperature (25 °C) were recorded with a Bruker Avance 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 spectrometer. 1H and ^{13}C NMR chemical shifts are given in ppm and referenced internally to residual non-deuterated solvent resonances.¹² The 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 $[(\text{Me}_3\text{Si})_2\text{N}(\text{H})\text{Si}(\text{Ph})_3]_2$ (1): Ph_3SiNH_2 (1.38 g, 5 mmol) was dissolved in hexanes (20 mL), then treated with a 2 M toluene solution of ZnMe_2 (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%. $\text{C}_{19}\text{H}_{19}\text{NSiZn}$ (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): $\delta_{\text{H}} = 7.74 - 7.63$ (br m, 6 H, C_6H_5), $7.34 - 7.16$ (br m, 9 H, C_6H_5), 0.01 (s, 1 H, NH), -0.31 (s, 3 H, ZnCH_3). ^{13}C $\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta_{\text{C}} = 138.5, 138.1, 130.5, 126.1$ (C_6H_5), -9.2 (ZnCH_3). ^{29}Si (99.35 MHz, C_6D_6): $\delta_{\text{Si}} = -11.9$.

Synthesis of $[(\text{Me}_3\text{Si})_2\text{N}(\text{H})\text{Si}(\text{NMe}_2)_3]_2$ (2): A solution of $(\text{Me}_2\text{N})_3\text{SiNH}_2$ (0.88 g, 5 mmol) in hexanes (10 mL) was treated with a 2 M toluene solution of ZnMe_2 (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%. $\text{C}_7\text{H}_{22}\text{N}_4\text{Si}_2\text{Zn}$ (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): $\delta_{\text{H}} = 2.45$ (s, 18 H, NCH_3), 0.16 (s, 1 H, NH), -0.25 (s, 3 H, ZnCH_3). ^{13}C $\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta_{\text{C}} = 38.6$ (NCH_3), -12.6 (ZnCH_3). ^{29}Si (99.35 MHz): $\delta_{\text{Si}} = -28.7$.

Synthesis of $[(\text{EtZnN}(\text{H})\text{Si}(\text{NMe}_2)_3]_2$ (3): A solution of $(\text{Me}_2\text{N})_3\text{SiNH}_2$ (0.35 g, 2 mmol) in hexanes (10 mL) was slowly treated with a 1 M solution of ZnEt_2 (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%. $\text{C}_8\text{H}_{24}\text{N}_4\text{Si}_2\text{Zn}$ (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): $\delta_{\text{H}} = 2.48$ (s, 18 H, NCH_3), 1.60 (t, 3 H, ZnCH_2CH_3 , $^3J_{\text{CH}_2\text{CH}_3} = 8.1$ Hz), 0.64 (q, 2 H, ZnCH_2CH_3 , $^3J_{\text{CH}_2\text{CH}_3} = 8.1$ Hz), 0.16 (s, 1 H, NH). ^{13}C $\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta_{\text{C}} = 38.7$ (NCH_3), 13.0 (ZnCH_2CH_3), 1.83 (ZnCH_2CH_3). ^{29}Si (99.35 MHz, C_6D_6): $\delta_{\text{Si}} = -28.9$.

Synthesis of $[(\text{Me}_3\text{Si})_2\text{N}(\text{H})\text{Si}(\text{Ph})_3]_2$ (4): Ph_3SiNH_2 (0.55 g, 2 mmol) was dissolved in hexanes (10 mL), then treated with a solution of $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ (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%. $\text{C}_{24}\text{H}_{34}\text{N}_2\text{Si}_3\text{Zn}$ (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): $\delta_{\text{H}} = 7.66 - 7.02$ (br m, 15 H, C_6H_5), $0.13 - 0.05$ (m, 13 H, SiCH_3), $-0.03 - -0.18$ (br m, 3 H, SiCH_3), $-0.19 - -0.36$ (br s, 2 H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (75.5 MHz, d_8 -THF): $\delta_{\text{C}} = 140.3, 136.6, 136.3, 129.9, 129.5, 128.4, 128.3$ (C_6H_5), 5.7 (SiCH_3). ^{29}Si (99.35 MHz, d_8 -THF): $\delta_{\text{Si}} = -5.0$ (SiMe_3), -16.1 (SiPh_3).

Synthesis of $[(\text{Me}_3\text{Si})_2\text{N}(\text{H})\text{Si}(\text{NMe}_2)_3]_2$ (5): A solution of $(\text{Me}_2\text{N})_3\text{SiNH}_2$ (0.71 g, 4 mmol) in hexanes (6 mL) was treated with a solution of $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ (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 redissolved with gentle heating. Crystallisation from the reaction solution at 5°C gave the product as colourless crystals. Yield: 1.07 g, 67%. $\text{C}_{12}\text{H}_{37}\text{N}_5\text{Si}_3\text{Zn}$ (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): $\delta_{\text{H}} = 2.55$ (s, 6 H, NCH_3), 2.50 (s, 12 H, NCH_3), 0.25 (s, 3 H, SiCH_3), 0.24 (s, 12 H, SiCH_3), 0.19 (s, 3 H, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta_{\text{C}} = 39.2$ (NCH_3), 5.6 (SiCH_3). ^{29}Si (99.35 MHz, C_6D_6): $\delta_{\text{Si}} = -3.9$ (SiMe_3), -28.1 (SiNMe_2).

Synthesis of $[(\text{Me}_3\text{Si})_2\text{N}]\{(\text{Me}_2\text{N})_3\text{SiN}(\text{H})\}[(\text{Me}_2\text{N})_3\text{SiN}]\text{Zn}_2$ (6): A solution of **5** (0.40 g, 0.5 mmol) in hexanes (10 mL) was treated with a solution of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (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): $\delta_{\text{H}} = 2.94 - 2.35$ (br m, NCH_3), $0.65 - 0.16$ (br m, SiCH_3). ^{13}C $\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta_{\text{C}} = 39.5, 39.0, 38.7$ (NCH_3), $6.4, 5.2, 2.6, 1.4$ (SiCH_3). ^{29}Si (99.35 MHz, C_6D_6): $\delta_{\text{Si}} = 2.4, -0.6$ (SiMe_3), $-20.2, -27.8, -31.1$ (SiNMe_2).

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- $\text{K}\alpha$ radiation ($\lambda = 0.71073$ 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 $\text{R}'\text{Zn}(\text{NH})\text{R}$ [$\text{R}' = \text{Me}$, $\text{R} = \text{SiPh}_3$ (**1**), $\text{R}' = \text{Me}$, $\text{R} = \text{Si}(\text{NMe}_2)_3$ (**2**); $\text{R}' = \text{Et}$, $\text{R} = \text{Si}(\text{NMe}_2)_3$ (**3**)] have been prepared by reaction of RNH_2 and $\text{R}'_2\text{Zn}$ in hexane. Similarly, $(\text{Me}_3\text{Si})_2\text{N}(\text{H})\text{R}$ [$\text{R} = \text{SiPh}_3$ (**4**), $\text{Si}(\text{NMe}_2)_3$ (**5**)] have been prepared analogously starting from $(\text{Me}_3\text{Si})_2\text{Zn}$ (Eqn 1):

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 ^1H 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 [$\delta = -0.31$ (**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 [$\delta = 0.01$ (**1**), 0.16 (**2**), 0.16 ppm (**3**)] that may be attributed to the remaining NH proton. Integration of these resonances show the $\{\text{R}_3\text{Si}\}$, $\{\text{ZnMe/Et}\}$ and $\{\text{NH}\}$ 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 ^1H NMR spectrum of **4** has a complex multiplet of signals corresponding to the four Me_3Si 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 ^1H NMR spectra of **5** shows two signals for the NMe_2 groups in 2:1 ratio consistent with the solid state structure incorporating the $\mu\text{-(NMe}_2\text{)Si(NMe}_2\text{)}_2$ moiety; there is also some non-equivalence to the Me_3Si 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 ^1H NMR spectrum.

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')-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 $\text{N(H)Si(NMe}_2)_3$ ligand, are dimeric but embody four-coordinated zinc atoms by virtue of both $\mu_2\text{-N(H)R}$ and $\mu_2\text{-NMe}_2$ moieties; the bulky $\text{Si(NMe}_2)_3$ groups are, as in **1**, **2**, in an *anti*-arrangement with respect to the central 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.

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 $\text{Zn}_2\text{N}_2\text{Si}$ ring [2.3377(14) - 2.4282(16) Å]. The Si-N bond associated with the $\mu_2\text{-NMe}_2$ 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 $\text{Zn}_2\text{N}_2\text{Si}$ rings.

In attempts to react the remaining N-H bond in these species to form bimetallic species, **5**, as representative, was treated with excess $\text{M[N(SiMe}_3)_2]$ ($\text{M} = \text{Li, K}$) or $\text{Zn[N(SiMe}_3)_2]_2$, but only starting materials could be isolated from these reactions. Remarkably, however, the stoichiometric reaction of **5** with $\text{Sn[N(SiMe}_3)_2]_2$ afforded the mixed amino-imido tetramer $\text{Zn}_4[\text{N(SiMe}_3)_2]_2[\text{NSi(NMe}_2)_3]_2[\text{N(H)Si(NMe}_2)_3]_2$ (**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 $\text{Zn}_4\text{Et}_2(\text{NHR})_4(\text{OEt})_2$ ($\text{R} = 2,6\text{-i-Pr}_2\text{C}_6\text{H}_3$).^{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. 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 Zn₆N₆ hexagonal drum with one Zn₂N₂ face missing. This is in contrast to the three fused rings in Zn₄Et₂(NHR)₄(OEt)₂ (R = 2,6-⁵Pr₂C₆H₃)^{3a} in which the two ZnOZnN rings are *anti* with respect to the central Zn₂O₂ 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 μ_3 -Zn₃ 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 Zn-N bonds are formed by the μ_2 -NMe₂ group [Zn(1')-N(2) 2.141(2) Å] and the terminal N(SiMe₃)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) 1.843(2) Å] and spanning the remaining, more typical Si-N bond lengths [1.708(3) – 1.731(2) Å]. The terminal N(SiMe₃)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 crowded to participate in any hydrogen bonding. Indeed, the crowding of these two functionalities is probably the reason why formation of the hexameric drum structure, typified by (iPrNAIH)₆¹⁷ 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 Me₃Si and Me₂N environments are broad and featureless, which reflects both the extent of non-equivalent environments and possible fluxionality. Similarly, the ¹³C NMR has 4 signals for the Me₃Si carbons and signals for two non-equivalent Me₃Si environments in the ²⁹Si NMR, while the

complexity of the SiNMe₂ environments is reflected in four ¹³C and three ²⁹Si NMR resonances. Additional peaks in the spectra can be attributed to residual **5** in the reaction mixture, which 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 experiments proved unsuccessful.

Conclusions

The synthesis of zinc (amido) complexes have been accomplished through protonolysis of either dialkyl-zinc or diamino-zinc starting materials with primary silyl-amide proligands. Despite successive attempts to force these complexes to undergo a double deprotonation of the amide proligand, zinc-imido species were not formed. In attempts to react the remaining N-H bond in these species to form bimetallic species, complex **5**, was treated the metal amides M[N(SiMe₃)₂] (M = Li, K) or excess Zn[N(SiMe₃)₂]₂, but only starting materials could be isolated from these reactions. Remarkably, reaction of **5** with Sn[N(SiMe₃)₂]₂ affords the unprecedented mixed amino-imido tetramer species Zn₄[N(SiMe₃)₂]₂[N-Si(NMe₂)₃]₂[N(H)Si(NMe₂)₃]₂ (**6**), albeit in very low yield (9%), in which the imido ligand has a μ_2 -bridging role and κ^2 -N,NMe₂ chelating coordination role. To the best of our knowledge, complex **6** represents the first zinc-imido species formed from a primary amine to have been identified and structurally 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 ₄ Si ₄ Zn ₄	C ₁₄ H ₄₄ N ₈ Si ₂ Zn ₂	C ₁₆ H ₄₈ N ₈ Si ₂ Zn ₂	C ₆₂ H ₈₄ N ₄ Si ₆ Zn ₂	C ₂₄ H ₇₄ N ₁₀ Si ₆ Zn ₂	C ₃₆ H ₁₁₀ N ₁₈ Si ₈ Zn ₄
Formula Mass	1511.38	511.49	539.54	1184.61	802.21	1281.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
<i>a</i> /Å	26.2840(3)	7.83400(10)	7.9730(2)	11.4310(4)	9.05200(10)	23.8580(4)
<i>b</i> /Å	9.4770(2)	10.0490(2)	18.1740(4)	11.9430(5)	21.7480(3)	18.2210(4)
<i>c</i> /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/Å ³	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	<i>Cc</i>	<i>P21/c</i>	<i>P21/n</i>	<i>P</i> $\bar{1}$	<i>P21/c</i>	<i>C2/c</i>
No. of formula units per unit cell, <i>Z</i>	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
<i>R</i> _{int}	0.0594	0.0569	0.0577	0.0549	0.0430	0.0599
Final <i>R</i> _i values (<i>I</i> > 2σ(<i>I</i>))	0.0489	0.0258	0.0273	0.0346	0.0308	0.0346
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1097	0.0666	0.0613	0.0786	0.0737	0.0758
Final <i>R</i> _i values (all data)	0.0731	0.0375	0.0393	0.0498	0.0397	0.0603
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1294	0.0732	0.0668	0.0853	0.0775	0.0848
Goodness of fit on <i>F</i> ²	1.014	1.055	1.093	1.047	1.077	1.040
CCDC number	960127	960128	960131	960129	960130	960132

Cite this: DOI: 10.1039/c0xx00000x

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^a Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. Fax: +44 1225 386231; Tel: +44 1225 384884; E-mail: a.l.johnson@bath.ac.uk

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