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Synthesis of zinc trisubstituted hydrazido complexes and *ortho*-metalation of 4-(dimethylamino)pyridine†

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The zinc hydrazide complexes $[EtZn(N(SiMe_3)NMe_2)]_2$, $[EtZn(N(Me)NMe_2)]_4$, and $Zn_3Et_4(N(Et)NMe_2)_2$ were synthesized by allowing excess hydrazine, $HN(R)NMe_2$, to react with diethyl zinc. The product of the reaction between $ZnEt_2$ and $HN(i\text{-}Pr)NMe_2$ *ortho*-metalated 4-(dimethylamino)pyridine (DMAP) at room temperature, producing the complex $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$. At elevated temperatures, $Zn_3Et_4(N(Et)NMe_2)_2$ also *ortho*-metalated DMAP, but $[EtZn(N(Me)NMe_2)]_4$ did not. Single-crystal X-ray diffraction studies revealed that the hydrazide ligands in $[EtZn(N(SiMe_3)NMe_2)]_2$ act as bridging mono-hapto amide ligands, and in $Zn_3Et_4(N(Et)NMe_2)_2$ and $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ the hydrazide ligands are di-hapto.

Introduction

Recently, we reported the syntheses of group 4 tetrakis(1-alkyl-2,2-dimethylhydrazido)metal complexes, $M(N(R)NMe_2)_4$ (M = Ti, R = Me; M = Zr or Hf, R = Me or Et), and the metal chloride derivatives $MCl(N(R)NMe_2)_3$ (M = Ti, R = Me; M = Zr, R = *i*-Pr or *t*-Bu; M = Hf, R = *t*-Bu), and $TaCl_3(N(i\text{-}Pr)NMe_2)_2$.[1,2] We also demonstrated that the tetrakis(trimethylhydrazido)zirconium and hafnium complexes were viable chemical vapor deposition precursors to metal oxide thin films.[3] As part of our synthetic studies of trialkylhydrazido metal complexes, we report herein the preparation of zinc complexes having trisubstituted hydrazide ligands and the unexpected *ortho*-metalation of 4-(dimethylamino)pyridine (DMAP) by two different zinc hydrazide derivatives.

Our work on the preparation of zinc hydrazide complexes is predated by the synthesis of $Zn(N(H)NH_2)_2$,[4] the first reported zinc hydrazide complex, and more recent comprehensive studies on zinc 1,1-dimethylhydrazide complexes, which included the syntheses of the tetrameric clusters $[RZn(N(H)NMe_2)]_4$ and $[RZn(N(H)N(CH_2)_n)]_4$ (R = Me, Et, or *i*-Pr; *n* = 4 or 5).[5–10] The incorporation of hydrazide ligands in zinc hexanuclear ring systems has also been reported.[11]

Experimental

General procedures and reagents

All manipulations were carried out in a glove box or by using Schlenk techniques. The solvents were purified according to standard methods and stored in the glove box over molecular sieves. Diethyl zinc was purchased from Aldrich and used as received. The hydrazines $HN(R)NMe_2$ (R = Me, Et, *i*-Pr, and $SiMe_3$) were prepared by following literature procedures.[2,12–15] Carbon-13 NMR spectra were collected in the proton decoupled mode, NMR coupling constants are in Hz, and ^1H and ^{13}C spectra were referenced internally to solvent resonances. Spectra were recorded on a 300-MHz instrument unless noted otherwise. Midwest Microlab, Indianapolis, IN USA performed the elemental analysis.

Synthesis of $[EtZn(N(SiMe_3)NMe_2)]_2$. 1-Trimethylsilyl-2,2-dimethylhydrazine (1.28 g, 9.72 mmol) was added dropwise to a solution of diethyl zinc (0.600 g, 4.86 mmol) in hexanes (25 mL). The mixture was stirred at room temperature for 12 h before the volatile components were removed under vacuum. The resulting residue was dissolved in triethylamine (3 mL), and the flask was placed in the freezer (–25 °C) for crystallization. Colorless crystals formed after 24 h. (Yield: 0.87 g, 79%). Found: C, 37.04; H, 8.45; N, 11.89. Calc. for $C_{14}H_{40}N_4Si_2Zn_2$: C, 37.25; H, 8.93; N, 12.41.

δ_H (C_6D_6): 0.25 (18 H, s, $N(Si(CH_3)_3)N(CH_3)_2$), 0.47 (4 H, q, J = 8, $ZnCH_2CH_3$), 1.42 (6 H, t, J = 8, $ZnCH_2CH_3$), 2.41 (12 H, s, $N(Si(CH_3)_3)N(CH_3)_2$). δ_C (C_6D_6): 2.38 ($N(Si(CH_3)_3)N(CH_3)_2$), 4.53 ($ZnCH_2CH_3$), 12.84 ($ZnCH_2CH_3$), 53.01 ($N(Si(CH_3)_3)N(CH_3)_2$). IR (Nujol, KBr, cm^{-1}): 1288 s, 1245 s, 1211 m, 1187 m, 1155 m, 1093 s, 1041 s, 1012 s, 995 w, 956 m, 919 m, 862 vs, 835 vs, 769 m, 754 m, 674 m.

Synthesis of $[EtZn(N(Me)NMe_2)]_4$. 1-Methyl-2,2-dimethylhydrazine (0.299 g, 4.04 mmol) was added dropwise to a solution of diethyl zinc (0.250 g, 2.02 mmol) in diethyl ether (25 mL). The mixture was stirred at room temperature for 12 h before the volatile components were removed under vacuum. The resulting white powder was dissolved in diethyl ether (3 mL), and the flask was placed in the freezer (–25 °C) for crystallization. Colorless crystals formed after 24 h. (Yield: 0.26 g, 77%). Found: C, 35.69; H, 8.15; N, 16.98. Calc. for $C_5H_{14}N_2Zn$: C, 35.84; H, 8.42; N, 16.72.

δ_H (600 MHz; C_6D_6): 0.063, 0.085, 0.094, 0.116, 0.185, 0.207, 0.237, 0.245, 0.267, 0.342 (8 H, q of dq, J = 8, $ZnCH_2CH_3$), 1.47 (3 H, t, J = 8, $ZnCH_2CH_3$), 1.585 (3 H, t, J = 8, $ZnCH_2CH_3$), 1.593 (3 H, t, J = 8, $ZnCH_2CH_3$), 1.69 (3 H, t, J = 8, $ZnCH_2CH_3$), 2.32 (3 H, s, $N(CH_3)N(CH_3)_2$), 2.336 (3 H, s, $N(CH_3)N(CH_3)_2$), 2.342 (3 H, s, $N(CH_3)N(CH_3)_2$), 2.36 (3 H, s, $N(CH_3)N(CH_3)_2$), 2.367 (3 H, s, $N(CH_3)N(CH_3)_2$), 2.372 (6 H, s, $N(CH_3)N(CH_3)_2$), 2.41

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(3 H, s, N(CH$_3$)N(C*H*$_3$)$_2$), 2.526 (3 H, s, N(C*H*$_3$)N(CH$_3$)$_2$), 2.531 (3 H, s, N(C*H*$_3$)N(CH$_3$)$_2$), 2.557 (3 H, s, N(C*H*$_3$)N(CH$_3$)$_2$), 2.562 (3 H, s, N(C*H*$_3$)N(CH$_3$)$_2$). δ_C (C_6D_6): –2.84, –2.35, –1.82, –0.64 (4 C, Zn*C*H$_2$CH$_3$), 15.01, 15.12, 15.25, 15.41 (4 C, ZnCH$_2$*C*H$_3$), 31.34, 31.77, 32.07, 32.43 (4 C, N(*C*H$_3$)N(CH$_3$)$_2$), 47.35, 47.66, 47.88, 47.92, 48.09, 48.28, 48.73, 48.79 (8 C, N(CH$_3$)N(*C*H$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 1305 m, 1234 m, 1205 s, 1189 m, 1155 s, 1118 m, 1083 s, 1047 m, 991 vs, 950 s, 916 m, 846 m, 765 s.

Synthesis of $Zn_3Et_4(N(Et)NMe_2)_2$. 1-Ethyl-2,2-dimethylhydrazine (0.426 g, 4.84 mmol) was added dropwise to a solution of diethyl zinc (0.300 g, 2.43 mmol) in diethyl ether (25 mL). The mixture was stirred at room temperature for 12 h before the volatile components were removed under vacuum. The resulting residue was dissolved in hexanes (3 mL), and the flask was placed in the freezer (–25 °C) for crystallization. Colorless crystals formed after 24 h. (Yield: 0.32 g, 82%). Found: C, 39.09; H, 8.65; N, 11.25. Calc. for $C_{16}H_{42}N_4Zn_3$: C, 39.48; H, 8.70; N, 11.51.

δ_H (C_6D_6): 0.41 (q, 8 H, *J* = 8, ZnC*H*$_2$CH$_3$), 1.08 (t, 6 H, *J* = 7, N(CH$_2$C*H*$_3$)N(CH$_3$)$_2$), 1.44 (t, 12 H, *J* = 8, ZnCH$_2$C*H*$_3$), 2.14 (s, 12 H, N(CH$_2$CH$_3$)N(C*H*$_3$)$_2$), 2.61 (q, 4 H, *J* = 7, N(C*H*$_2$CH$_3$)N(CH$_3$)$_2$). δ_C (C_6D_6): 2.01 (Zn*C*H$_2$CH$_3$), 13.02 and 14.02 (N(CH$_2$*C*H$_3$)N(CH$_3$)$_2$) or (ZnCH$_2$*C*H$_3$), 36.34 (N(*C*H$_2$CH$_3$)N(CH$_3$)$_2$), 46.74 (N(CH$_2$CH$_3$)N(*C*H$_3$)$_2$). IR (Nujol, KBr, cm^{-1}): 1397 s, 1348 s, 1242 m, 1231 m, 1208 m, 1183 m, 1137 s, 1111 vs, 1080 m, 1044 vs, 998 vs, 990 vs, 949 vs, 917 s, 784 vs, 668 w.

Synthesis of Zn[(NC$_5$H$_3$-*p*-NMe$_2$)ZnEt(N(*i*-Pr)NMe$_2$)]$_2$. 1-Isopropyl-2,2-dimethylhydrazine (0.496 g, 4.86 mmol) was added dropwise to a solution of diethyl zinc (0.300 g, 2.43 mmol) in diethyl ether (25 mL). The mixture was stirred at room temperature for 12 h before the volatile components were removed under vacuum. The residue was dissolved in diethyl ether, and DMAP (0.198 g, 1.62 mmol) was added to the solution. After stirring the reaction mixture for 12 h, the volume of diethyl ether was reduced (~ 5 mL), and the flask was placed in the freezer (–25 °C) for crystallization. Crystals of DMAP and the product formed. The crystals were separated from the mother liquor, whereupon they were washed (3 × 5 mL) with cold (0 °C) pentane. The pentane wash solution was collected, the solution was reduced in volume under vacuum (~3 mL), and the flask was placed in the freezer for crystallization. Crystals of the product formed after a few hours. (Yield: 0.41 g, 73%). Found: C, 47.64; H, 7.43; N, 15.78. Calc. for $C_{28}H_{54}N_8Zn_3$: C, 48.11; H, 7.79; N, 16.03.

δ_H (C_6D_6): 0.63 and 0.68 (q of dq, 2 H, ^3J = 8 and ^2J = 13, ZnC*H*$_2$CH$_3$), 0.74 and 0.78 (q of dq, 2 H, ^3J = 8 and ^2J = 13, ZnC*H*$_2$CH$_3$), 1.24 and 1.26 (d, 12 H, *J* = 7, N(CH(C*H*$_3$)$_2$)), 1.92 (t, 6 H, *J* = 8, ZnCH$_2$C*H*$_3$), 2.19 (s, 6 H, NN(C*H*$_3$)$_2$), 2.33 (s, 12 H, NC$_5$H$_3$(N(C*H*$_3$)$_2$)), 2.86 (s, 6 H, NN(C*H*$_3$)$_2$), 3.48 (sept, 2 H, *J* = 7, N(CH(C*H*$_3$)$_2$)), 6.00 and 6.03 (d of d, 2 H, ^3J = 7 and ^4J = 3, *p*-H to Zn), 7.311 and 7.314 (d of d, 2 H, ^4J = 3 and ^5J = 1, *o*-H to Zn), 8.313 and 8.316 (d of d, 2 H, ^3J = 7 and ^5J = 1, *m*-H to Zn). δ_C (C_6D_6): 0.74 (Zn*C*H$_2$CH$_3$), 15.2 (ZnCH$_2$*C*H$_3$), 27.9 (N(CH(*C*H$_3$)$_2$)), 28.4 (N(CH(*C*H$_3$)$_2$)), 38.3 (NC$_5$H$_3$-*p*-N(*C*H$_3$)$_2$), 45.9 and 46.5 (NN(*C*H$_3$)$_2$), 51.0 (N(*C*H(CH$_3$)$_2$)), 104.3, 117.2, 147.2, 151.7, and 198.8 (N*C*$_5$H$_3$). IR (Nujol, NaCl, cm^{-1}): 1602 vs, 1536 m, 1519 m, 1446 vs, 1346 w, 1225 vs, 1104 w, 1068 w, 1041 w, 1016 w, 988 s, 947 w, 807 s, 767 w, 751 w, 663 w.

Crystal structure determinations

Single-crystal X-ray diffraction data were collected for crystals of [EtZn(N(SiMe$_3$)NMe$_2$)]$_2$ (colorless, prismatic block), Zn$_3$Et$_4$(N(Et)NMe$_2$)$_2$ (colorless, irregular block), and Zn[(NC$_5$H$_3$-*p*-NMe$_2$)ZnEt(N(*i*-Pr)NMe$_2$)]$_2$·OEt$_2$ (colorless, diamond plate). Crystal data are presented in Table 1. All measurements were made with a Siemens SMART platform diffractometer equipped with a CCD area detector. The programs used in the X-ray diffraction analyses were as follows: Data collection, Siemens APEX2 v1.0–27 (Bruker-Nonius, 2005); cell refinement and data reduction, Bruker SAINT v7.12A (Bruker-Nonius, 2004); structure solution, SHELXS v6.12 (G. M. Sheldrick, 2001); and structure refinement, SHELXL v6.12 (G. M. Sheldrick, 2001).

In [EtZn(N(SiMe$_3$)NMe$_2$)]$_2$ the ethyl group was disordered over two slightly different positions. The molecule Zn$_3$Et$_4$(N(Et)NMe$_2$)$_2$ was massively disordered about a two-fold axis such that the actual connectivity was ambiguous. The model

Table 1 Crystal data for [EtZn(N(SiMe$_3$)NMe$_2$)]$_2$, Zn$_3$Et$_4$(N(Et)NMe$_2$)$_2$, and Zn[(NC$_5$H$_3$-*p*-NMe$_2$)ZnEt(N(*i*-Pr)NMe$_2$)]$_2$·OEt

	[EtZn(N(SiMe$_3$)NMe$_2$)]$_2$	Zn$_3$Et$_4$(N(Et)NMe$_2$)$_2$	Zn[(NC$_5$H$_3$-*p*-NMe$_2$)ZnEt(N(*i*-Pr)NMe$_2$)]$_2$·OEt$_2$
Chemical formula	$C_{14}H_{40}N_4Si_2Zn_2$	$C_{16}H_{42}N_4Zn_3$	$C_{32}H_{64}N_8OZn_3$
Formula weight	451.42	486.65	773.02
Crystal dim./mm	0.45 × 0.35 × 0.30	0.30 × 0.25 × 0.25	0.50 × 0.30 × 0.20
Crystal system	Triclinic	Tetragonal	Monoclinic
Space group	$P\bar{1}$	$P4_32_12$	$I2/a$
a/Å	8.0256(6)	9.2341(4)	24.5861(11)
b/Å	9.0317(7)	9.2341(4)	12.0656(4)
c/Å	9.4274(7)	27.1810(18)	27.1240(10)
α (°)	109.784(1)	90	90
β (°)	107.771(1)	90	106.337(1)
γ (°)	97.884(1)	90	90
T/K	223(2)	223(2)	223(2)
Z	1	4	8
V/Å^3	589.87(8)	2317.7(2)	7721.3(5)
D_{calcs}/g cm^{-3}	1.271	1.395	1.330
μ/mm^{-1}	2.137	3.084	1.883
Reflections measured/unique	3012/2069	11040/1888	19494/7176
R_{int}	0.0160	0.0268	0.0220
R_1, wR_2 ($I > 4\sigma(I)$)	0.0227, 0.0587	0.0233, 0.0571	0.0244, 0.0657

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finally chosen represented the best guess of the atomic arrangement. Only the zinc atoms were refined anisotropically. The asymmetric unit of $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2\cdot OEt_2$ consisted of one molecule in a general position, and two half-molecules of diethyl ether solvent disordered about a two-fold axis. Both of the ethyl groups attached to Zn were disordered; they were refined using distant constraints with occupancy factors estimated based on comparison of isotropic displacement parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC 784270, 784271, and 784272 for $[EtZn(N(SiMe_3)NMe_2)]_2$, $Zn_3Et_4(N(Et)NMe_2)_2$, and $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2\cdot OEt_2$, respectively). Copies of the data can be obtained, free of charge, *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

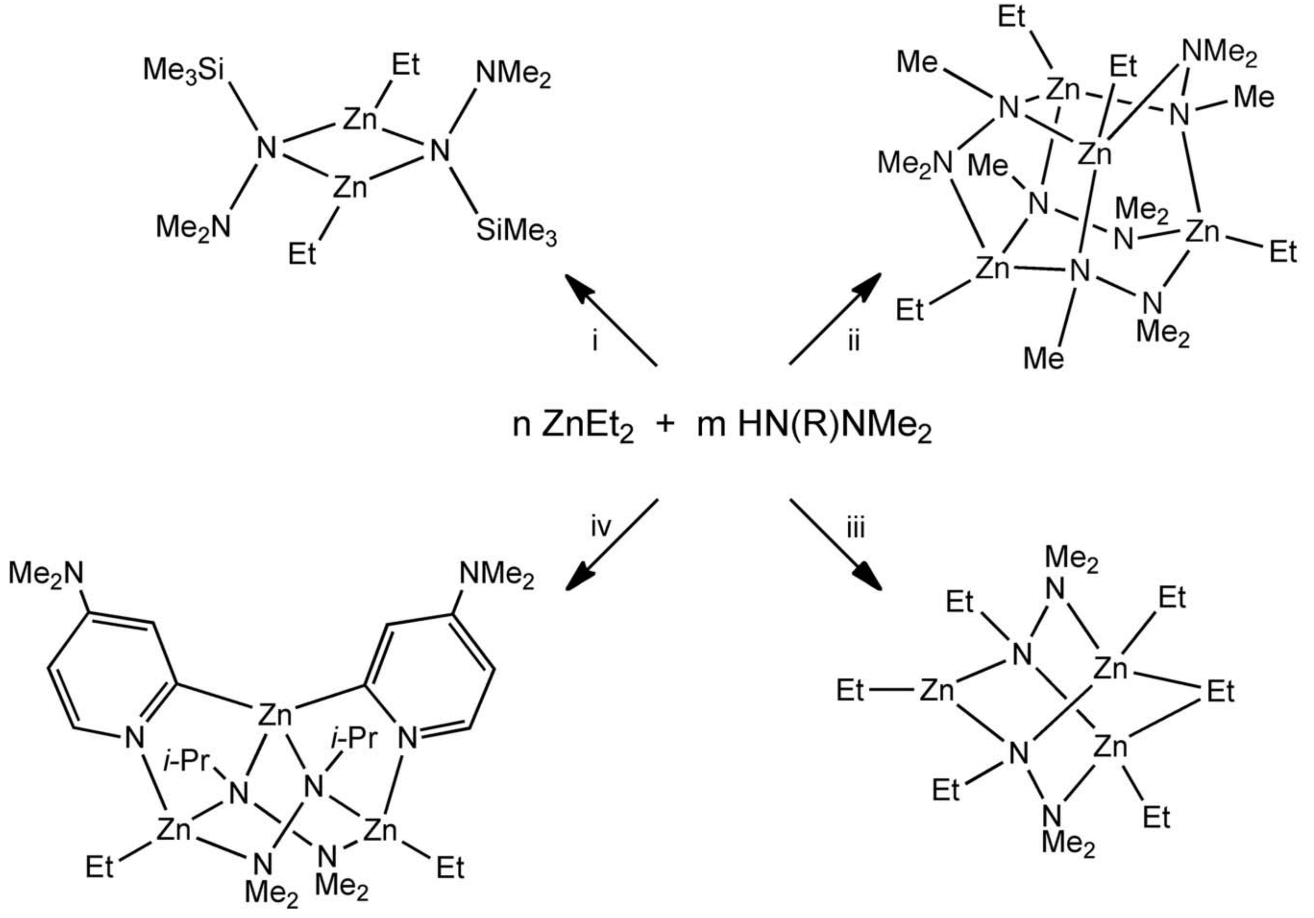
Results and discussion

Synthesis

A summary of our synthetic results is presented in Scheme 1.

Diethyl zinc reacted with excess $HN(R)NMe_2$ (R = $SiMe_3$ or Me) to produce the dimer $[EtZn(N(SiMe_3)NMe_2)]_2$ and tetramer $[EtZn(N(Me)NMe_2)]_4$ in 70–80% crystalline yield. Excess hydrazine was used in the syntheses to minimize the amount of unreacted diethyl zinc in the product mixtures. In contrast, diethyl zinc reacted with excess $HN(Et)NMe_2$ to produce $Zn_3Et_4(N(Et)NMe_2)_2$, a product of incomplete ethyl ligand replacement by hydrazide ligand. Isolated yields of crystalline $Zn_3Et_4(N(Et)NMe_2)_2$ were reproducibly about 70%. An attempt to obtain $[EtZn(N(Et)NMe_2)]_n$ by stirring $ZnEt_2$ and excess $HN(Et)NMe_2$ in refluxing diethyl ether failed, yielding only $Zn_3Et_4(N(Et)NMe_2)_2$ according to a ^{1}H NMR spectrum of the products.

Given the incomplete ethyl ligand replacement when $HN(Et)NMe_2$ was reacted with $ZnEt_2$, we expected that the reaction between $ZnEt_2$ and the more bulky hydrazine $HN(i\text{-}Pr)NMe_2$ would result similarly in incomplete substitution. We were surprised to find, however, that the reaction yielded a thermally unstable, waxy solid that analyzed as $EtZnN(i\text{-}Pr)NMe_2$ by using ^{1}H NMR integration. After repeated failed attempts to obtain a single crystal of the product suitable for an X-ray diffraction study or to purify the material enough to obtain a consistent combustion analysis, we sought to synthesize a DMAP adduct of the product for characterization. Unexpectedly, this effort produced the *ortho*-metalated DMAP complex $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$. Presumably, the coordination of DMAP to zinc activated DMAP to *ortho* deprotonation.[16,17]



Scheme 1 Summary of the synthetic studies. (i) R = $SiMe_3$, $n = m = 2$, –2EtH; (ii) R = Me, $n = m = 4$, –4EtH; (iii) R = Et, $n = 3$, $m = 2$, –2EtH; (iv) R = *i*-Pr, $n = 3$, $m = 2$, +2DMAP, –4EtH.

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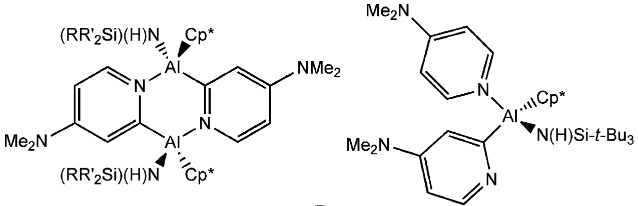
The unexpected *ortho*-metalation of DMAP prompted us to attempt DMAP metalation with other zinc reagents. No metalation was observed when $ZnEt_2$ (neat) and DMAP were mixed (23 °C, 4 h), nor was there metalation when $[EtZn(N(Me)NMe_2)]_4$ and DMAP were mixed in diethyl ether (23 °C, 12 h) or when the reagents were heated in benzene-d_6 (60 °C, 12 h). There was clear NMR evidence for *ortho*-metalation of DMAP, however, after $Zn_3Et_4(N(Et)NMe_2)_2$ and DMAP were heated in benzene-d_6 (60 °C, 12 h) and after they were allowed to react in refluxing diethyl ether (12 h). It is possible that when the waxy product and $Zn_3Et_4(N(Et)NMe_2)_2$ are in solution, they produce analogous reactive species that do the *ortho*-metalation. Ortho-metalation of DMAP, while not common, has been reported using lithium,[16] aluminium (**I**),[18] zirconium,[19,20] and dialkyl-tetramethylpiperidide-zincate reagents.[21–23] The hydrazide complex EtZnN(*i*-Pr)NMe_2 represents a new zinc-based system for *ortho*-metalation of DMAP under mild conditions in which alkali metal mediation is not required for metalation.[21]



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The complexes $[EtZn(N(Me)NMe_2)]_4$, $Zn_3Et_4(N(Et)NMe_2)_2$, and $[EtZn(N(SiMe_3)NMe_2)]_2$ sublimed (110, 75, and 85 °C/0.02 mm Hg, respectively) without decomposition. All the complexes were extremely soluble in hydrocarbon solvents, diethyl ether, and THF. Attempts to prepare homoleptic complexes $Zn(N(R)NMe_2)_2$ for R = Me, Et, *i*-Pr, and $SiMe_3$ by reacting $ZnEt_2$ with $HN(R)NMe_2$ in hot toluene solvent (120 °C/sealed pressure flask) were unsuccessful.

Single crystal X-ray diffraction studies. The crystal structures of $[EtZn(N(SiMe_3)NMe_2)]_2$ (Fig. 1), $Zn_3Et_4(N(Et)NMe_2)_2$ (Fig. 2), and $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ (Fig. 3) were determined. Selected bond lengths and angles for $[EtZn(N(SiMe_3)NMe_2)]_2$ are presented in the Fig. 1 caption and for $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ in Table 2. Molecules of $Zn_3Et_4(N(Et)NMe_2)_2$ were found to be severely disordered in the crystal. Only the overall structure, illustrated by the ball-and-stick plot in Fig. 2, could be determined from the refinement; the bond lengths and angles are not reliable and will not be discussed.

The complex $[EtZn(N(SiMe_3)NMe_2)]_2$ (Fig. 1) has a crystallographically imposed center of inversion. In the complex, the hydrazide ligands act as anionic mono-hapto amide ligands analogous to the bridging amide ligands in $[Zn(NR_2)(\mu\text{-}NR_2)]_2$ (R = CH_2Ph or *i*-Bu).[24,25] The geometry at Zn is distorted trigonal planar with the trigonal plane defined by the methylene carbon atom and two N_{amide} atoms (Σ(X–Zn–Y) ≈ 360°).

The structure of $Zn_3Et_4(N(Et)NMe_2)_2$ (Fig. 2) consists of one three-coordinate zinc atom (Zn3 in Fig. 2) and two four-coordinate zinc atoms. The molecule would have virtual C_2 symmetry if the terminal ethyl ligand on Zn3 and the bridging ethyl ligand were excluded. One way to view the geometry is to note that Zn1, Zn2, N1, N2, N3, and N4 define a six-member ring. The atoms Zn1 and Zn2 are linked on one side of the six-member ring by the μ-Et group, thereby forming two fused five-member rings, and N1 and N3 are linked on the opposite side of the six-member ring *via* Zn3, thereby forming two additional five-member rings. The

Table 2 Selected bond lengths (Å) and angles (°) for $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2\cdot OEt_2$

Zn1–C1	2.001(5)
Zn2–C15	1.995(4)
Zn1–N1	2.0502(17)
Zn2–N5	2.0607(17)
Zn1–N3	2.0902(19)
Zn2–N7	2.0816(17)
Zn1–N6	2.1974(18)
Zn2–N2	2.2042(18)
Zn3–C22	2.023(2)
Zn3–C8	2.032(2)
Zn3–N1	2.1798(17)
Zn3–N5	2.1814(17)
C1–Zn1–N1	137.8(2)
C1–Zn1–N3	108.4(2)
N1–Zn1–N3	93.72(7)
N6–Zn1–C1	113.1(2)
N6–Zn1–N1	99.39(6)
N6–Zn1–N3	95.68(7)
C15–Zn2–N5	136.7(2)
C15–Zn2–N2	106.84(18)
N7–Zn2–C15	117.8(2)
N7–Zn2–N5	93.27(7)
N5–Zn2–N2	98.77(7)
N7–Zn2–N2	95.37(7)
C22–Zn3–C8	145.22(8)
C22–Zn3–N1	108.38(7)
C8–Zn3–N1	96.50(7)
C22–Zn3–N5	95.78(7)
C8–Zn3–N5	107.86(7)
N1–Zn3–N5	91.24(6)

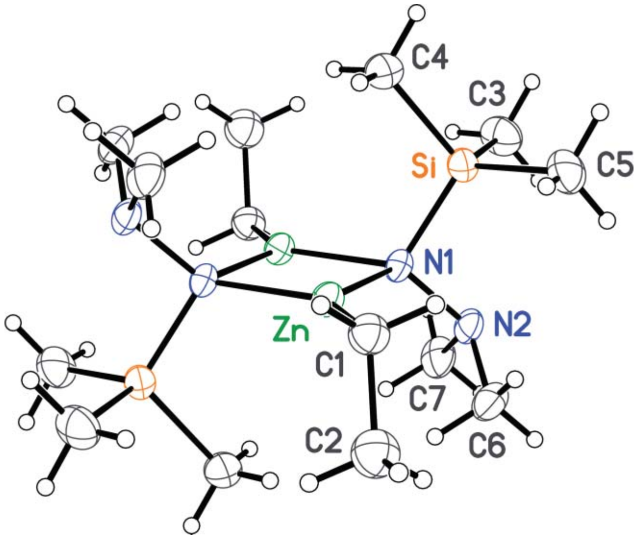

Fig. 1 View of $[EtZn(N(SiMe_3)NMe_2)]_2$ showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes. Only one orientation of the disordered ethyl group is shown. Selected bond lengths (Å) and angles (°): Zn–C1 1.960(6), Zn–N1 2.0469(17), Zn–N1′ 2.0592(17), C1–Zn–N1 132.9(2), C1–Zn–N1′ 135.6(2), N1–Zn–N1′ 91.48(6), Zn–N1–Zn 88.52(6), Zn–N1–N2 121.12(12), Zn–N1–Si 114.24(9), N2–N1–Si 99.19(12).

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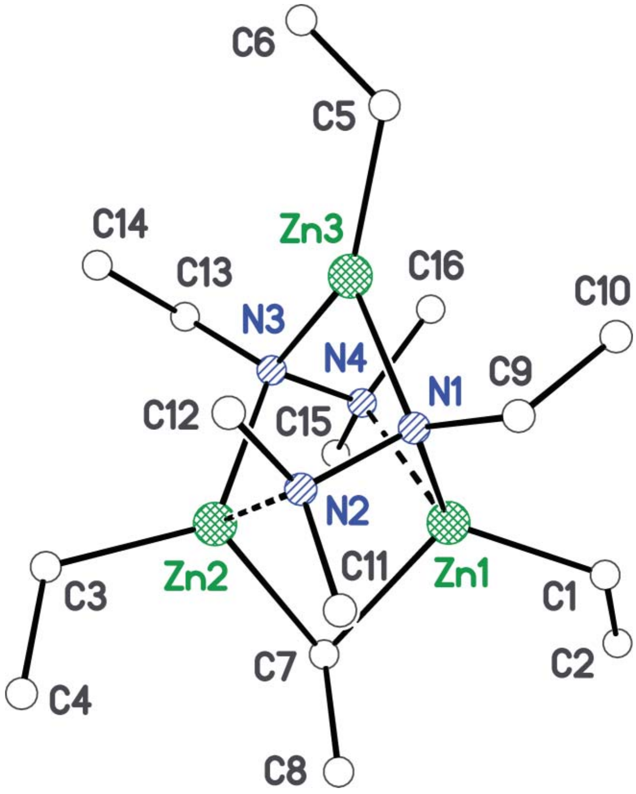


Fig. 2 Ball-and-stick plot of $Zn_3Et_4(N(Et)NMe_2)_2$ showing the overall structure. The plot represents only one of many possible orientations of the ligands that fit the data.

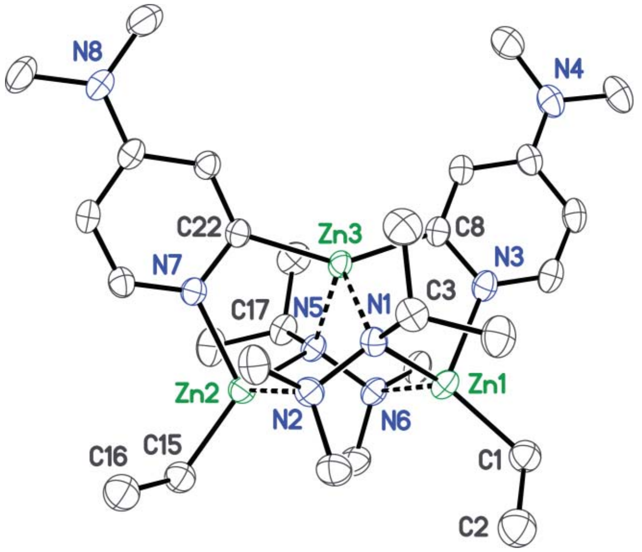
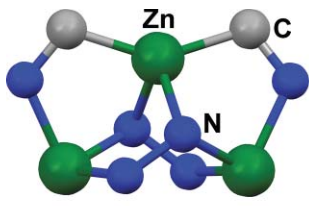


Fig. 3 View of $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ showing the atom-numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted. Only one orientation of each disordered ethyl group is shown.

bridging ethyl ligand in $Zn_3Et_4(N(Et)NMe_2)_2$ is one of only a few examples of a bridging alkyl ligand in structurally characterized zinc complexes.[26,27]

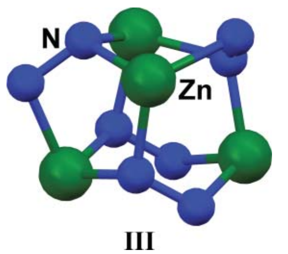
In $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ (Fig. 3), two Zn, two N_{amide}, and two N_{amine} atoms define a boat-shaped six-member ring. The two Zn atoms in the six-member ring are each coordinated to a DMAP ring nitrogen, and the third Zn atom in the structure is attached to an *ortho* carbon of each DMAP and to both N_{amide} atoms in the six-member ring. The effect is to create a fused ring structure consisting of five and six-member rings, as illustrated in **II**. The geometry at Zn1 and Zn2 may be described as distorted trigonal pyramidal with the pyridine fragment N3 and N7 atoms, respectively, occupying the apical positions, and the geometry at Zn3 may be described as distorted see-saw with C8–Zn3–C22 = 145° and N1–Zn3–N5 = 91°.



II

The Zn–N distances in $[EtZn(N(SiMe_3)NMe_2)]_2$ (2.0469(17) and 2.0592(17) Å) and Zn1–N1 and Zn2–N5 distances in $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ (2.0502(17) and 2.0607(17) Å) are comparable to the bridging $Zn–N_{amide}$ distances in $[RZn(NHNMe_2)]_4$ (R = Et or *i*-Pr, range 2.039(7)–2.098(3) Å)[5–7] and $[Zn(NR_2)(\mu\text{-}NR_2)]_2$ (R = CH_2Ph, av. 2.0352(13) Å; R = *i*-Bu, av. 2.028(2) Å).[24,25] The Zn1–N6, Zn2–N2, Zn3–N1, and Zn3–N5 distances in $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ (2.1798(17)–2.2042(18) Å) are similar to the $Zn–N_{amine}$ distances in $[RZn(NHNMe_2)]_4$ (R = Et or *i*-Pr, 2.150(3)–2.192(3) Å)[5–7] but are shorter than those in the simpler amine adducts $Zn[(CH_2)_3NMe_2]_2$ (2.307(4) Å),[28] $ZnMe_2[cyclo\text{-}(CH_2NMe)_3]_2$ (2.410(4) Å),[29] and $ZnEt_2(Et_2NCH_2CH_2NEt_2)$ (av. 2.263(2) Å).[30] The Zn–N(DMAP) distances in $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ (av. 2.0859(19) Å) appear normal when compared to the analogous distances in $[ZnMe(O_2CNR_2)(py)]_2$ (R = *i*-Pr and *i*-Bu, av. 2.121(2) Å),[31] $ZnMe_2(DMAP)_2$ (av. 2.023(2) Å),[32] and $[Zn(t\text{-}Bu)_2(1,2\text{-bis}(4\text{-pyridyl})ethane)]_n$ (2.220(3) Å).[33] The Zn–C(DMAP) distances, 2.023(2) and 2.032(2) Å, are close to the range of $Zn–C(4\text{-}R\text{-}C_5H_3N)$ distances found in the *ortho*-zincated complexes $[\{2\text{-}Zn(Et)_2\text{-}\mu\text{-}4\text{-}R\text{-}C_5H_3N\}_2\cdot 2\{K(N,N,N',N'',N''\text{-pentamethyldiethylenetriamine})\}]$ where R = NMe_2, H, Et, *i*-Pr, *t*-Bu, and Ph ((2.067–2.1007 Å).[23]

A single-crystal X-ray diffraction study of $[EtZn(N(Me)NMe_2)]_4$ was also performed, but the structure could not be solved satisfactorily because of disorder. The primary molecular component in crystals of $[EtZn(N(Me)NMe_2)]_4$ closely resembles the structures of $[RZn(N(H)NMe_2)]_4$ (R = Et or *i*-Pr),[5–7] wherein the core consists of two fused six-member rings, one in a chair confirmation and the other in a boat confirmation, and four fused five-member rings, as illustrated in **III** and Scheme 1. Each zinc atom and nitrogen atom is four-coordinate.



III

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Solution characterization. In the solid state, $[EtZn(N(SiMe_3)NMe_2)]_2$ has a crystallographically imposed center of inversion. If the structure is maintained in solution, the NMe_2 groups should give rise to two singlets and the methylene protons of the ethyl ligands should give rise to a doublet of quartets. The ^1H NMR spectra recorded at room temperature and at –70 °C, however, revealed only two singlets, one triplet, and one quartet, indicating a low energy fluxional process occurs that renders the amine methyl protons and ethyl methylene protons equivalent. A monomer-dimer equilibrium is a possible explanation for the dynamic behavior, or the molecule might adopt a geometry in solution in which the hydrazide ligand substituents have a *syn* relationship, resulting in virtual C_{2v} symmetry and equivalent amine methyl protons and ethyl methylene protons.

The $^{13}C\{^1H\}$ spectrum of the tetramer $[EtZn(N(Me)NMe_2)]_4$ at room temperature reveals four resonances in each of the NMe, $ZnCH_2CH_3$, and $ZnCH_2CH_3$ regions and eight resonances in the NMe_2 region, which is ostensibly consistent with the proposed solid state structure. The ^1H NMR spectrum at room temperature, however, reveals eleven singlets in the NMe and NMe_2 regions (there is one apparent accidental degeneracy), four well-resolved triplets in the $ZnCH_2CH_3$ region, and at least ten quartets in the $ZnCH_2CH_3$ region. To be consistent with the proposed solid-state structure, there should be eight doublets of quartets (or sixteen quartets) in the $ZnCH_2CH_3$ region. Furthermore, one of the ten observed $ZnCH_2CH_3$ quartets (δ 0.342) has a relative intensity consistent with two protons, but there are no quartets within 12–14 Hz of this quartet, as expected for doublet of quartet resonances. A fluxional process cannot explain the discrepancies in the ^1H NMR spectrum; thus, it is likely there are equilibria involved. Mitzel *et al.* alluded to a similar possibility when they described the spectra of $[RZn(N(H)NMe_2)]_4$ (R = Me or Et).[5]

The room temperature ^1H NMR spectrum of $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ is consistent with the virtual C_2 symmetry found in the solid-state structure. Thus, for example, the hydrazide ligand NMe_2 groups and $CHMe_2$ substituents give rise to two singlets and two doublets, respectively, and the ethyl ligand CH_2 groups give rise to two doublets of quartets.

Spectra recorded for $Zn_3Et_4(N(Et)NMe_2)_2$ at room temperature and –50 °C indicate the molecule is fluxional, revealing only resonances consistent with one type of ethyl ligand and one type of hydrazide ligand. Importantly, however, the integration is consistent with the stoichiometry found in the solid-state structure and by chemical analysis (*i.e.*, the integral ratio Et:N(Et)NMe_2 is 2 : 1).

Conclusion

The zinc hydrazide complexes $[EtZn(N(SiMe_3)NMe_2)]_2$ and $[EtZn(N(Me)NMe_2)]_4$, were synthesized from diethyl zinc and excess of the respective hydrazines, but under similar conditions and using 1-ethyl-2,2-dimethylhydrazine the cluster $Zn_3Et_4(N(Et)NMe_2)_2$ was obtained. At elevated temperatures, the cluster $Zn_3Et_4(N(Et)NMe_2)_2$, and at room temperature, the product of the reaction between $ZnEt_2$ and $HN(i\text{-}Pr)NMe_2$, both *ortho*-metalated DMAP. In the latter case, zincated product $Zn[(NC_5H_3\text{-}p\text{-}NMe_2)ZnEt(N(i\text{-}Pr)NMe_2)]_2$ was isolated and structurally characterized. Studies to determine whether these and analogous zinc hydrazide reagents can metalate pyridine derivatives other than DMAP are in progress.

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