Synthesis and structures of bimetallic and polymeric zinc coordination compounds supported by salicylaldiminato and anilido–aldimine ligands†

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A series of bimetallic zinc complexes bearing salicylaldiminato (**1b–3b**) or anilido–aldimine (**4c–5c**) ligand frameworks, in which the metal centres are separated by aliphatic spacer groups containing 3–6 methylene units, were targeted. X-Ray analysis of salicylaldiminato derivative **2b**, with a 4 carbon spacer group, revealed a coordination polymer in the solid state where each zinc centre is ligated by two salicylaldiminato ligands. Contrastingly, the structure of the anilido–aldimine complex **4c**, with a 3 carbon methylene spacer group, was found to be a discrete bimetallic complex. These differences are attributed to the differing steric protection at the anilido *vs* phenoxy donors, the latter more readily facilitating bridges between metal centres.

Introduction

Catalytic pathways involving the cooperative reactivity between two mutually interconnected metal complexes has been observed in nature. One such example is the phosphomonoesterase enzyme alkaline phosphatase which is known to contain two Zn centres at the active site.[1] Consequently, much attention has been directed toward the synthesis of bimetallic zinc complexes which can potentially mimic phosphomonoesterase activity in protic media.[2,3]

Contrastingly, organometallic binuclear zinc complexes that are soluble in aprotic media are less commonly encountered.[4,5] In addition to their structural novelty, these complexes also have potential applications in conventional catalysis. For example, Coates and co-workers have shown that the copolymerisation of cyclohexene oxide with the biorenewable feedstock CO_2, catalysed by β-diminiminate zinc complexes, occurs *via* a bimetallic intermediate involving the cooperative effect of two discrete Zn species.[6] Further studies have suggested that bimetallic analogues of such β-diminiminate zinc complexes can provide an enhancement of catalytic activity over their monometallic derivatives.[7] It has also been proposed that zinc centres held at a certain fixed distance apart, such as found in the zinc glutarate lattice, are beneficial for copolymerisations of propylene oxide with carbon dioxide.[8] With these considerations in mind, we initiated a study to investigate the synthesis and charaterisation of bimetallic salicylaldiminato Zn complexes and anilido–aldimine zinc complexes in which the ligated zinc centres are separated by aliphatic methylene spacer groups of between 3–6 carbon atoms to allow for differing separation of the two metal centres.

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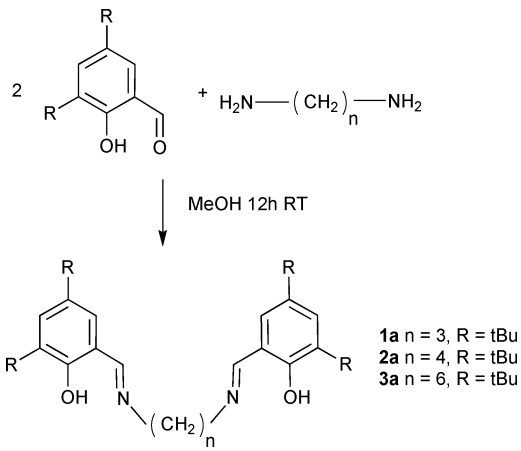
† Electronic supplementary information (ESI) available: Crystal data for **2b**, **4c** and **5c**; selected bond lengths and angles for **5c**; structures of **2b**, **4c** and **5c** and environment of the Zn_2O_2 ring in the structure of **2b**. See DOI: 10.1039/b615080b

Results and discussion

Bis-salicylaldiminato complexes

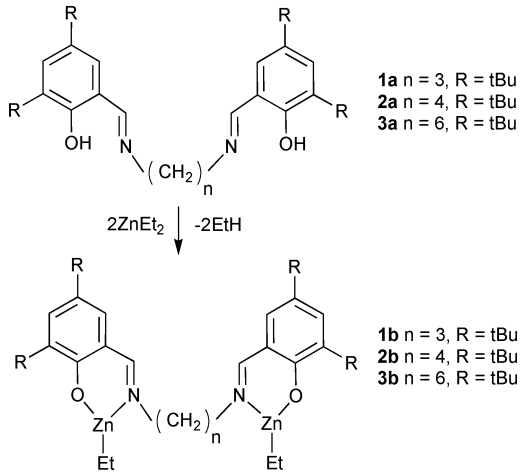
The pro-ligands **1a**, **2a** and **3a** were prepared by standard condensation reactions between two equivalents of 3,5-^{t}Bu salicylaldehyde and one equivalent of the appropriate diamine in methanol (Scheme 1).



Scheme 1 Synthesis of **1a–3a**.

The ligands were isolated in high yield and were recrystallised from pentane. ^{1}H-NMR and ^{13}C-NMR studies gave well resolved resonances for all proton and carbon environments, while elemental analysis indicated that the compounds were formed in good purity.

Compounds **1b–3b** were prepared by the reaction of two equivalents of $ZnEt_2$ with one equivalent of the pro-ligands **1a–3a**, respectively, in toluene (Scheme 2). They were recrystallised from toluene, pentane or mixtures of both to give bright yellow (**1b**, **2b**) and pale yellow (**3b**) crystalline aggregates. X-Ray quality crystals of **2b** could be obtained from a 50 : 50 toluene–pentane mixture after standing for 6 days at −25 °C.



Scheme 2 Synthesis of **1b–3b**.

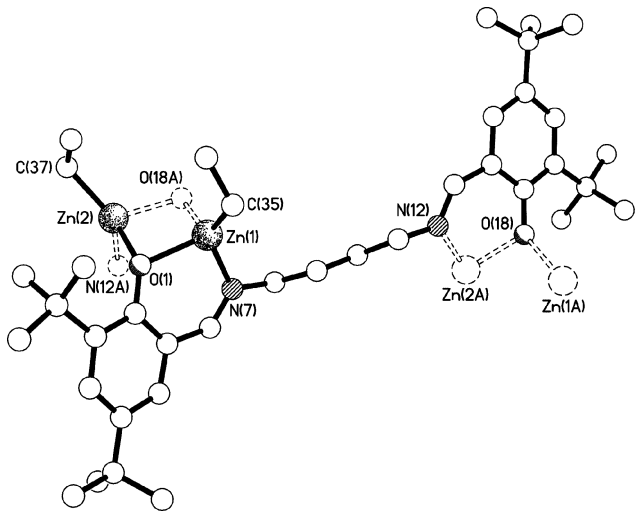


Fig. 1 The asymmetric unit in the structure of **2b**. Atom labels with an "A" after the number are related to their counterparts without the letter by a glide plane, *e.g.* Zn(1) and Zn(1A).

The single crystal X-ray structure determination on **2b** revealed the formation of an extended polymer with the bis(salicylaldiminato) ligand linking neighbouring Zn_2O_2 rings; Fig. 1 shows the basic repeating moiety (the crystallographic asymmetric unit) and Fig. 2 shows part of one of the polymer chains.

The Zn_2O_2 rings have a slightly folded geometry, the $\{Zn_2O(1)\}$ and $\{Zn_2O(18)\}$ planes being inclined by *ca.* 14°; the transannular Zn···Zn and O···O distances are 3.0276(5) and 2.817(3) Å respectively. The geometries at the zinc centres are distorted tetrahedral with angles in the range 85.49(9)–131.70(15)° at Zn(1), and 85.48(9)–132.15(19)° at Zn(2) (Table 1). The O(1)/N(7) and O(18)/N(12) six-membered C_3NOZn chelate rings both adopt folded geometries. For the former Zn(1) and N(7) lie *ca.* 0.92 and 0.41 Å respectively out of the $\{C_3O\}$ plane (which is coplanar to within *ca.* 0.04 Å) in a direction away from Zn(2), whilst for the latter Zn(2A) and N(12) lie *ca.* 0.87 and 0.34 Å respectively out of the $\{C_3O\}$ plane (which is coplanar to within *ca.* 0.01 Å) in a direction away from Zn(1). The ethyl ligands on each zinc centre are in a *syn* relationship (see Fig. S2 in the ESI†) such that

Table 1 Selected bond lengths (Å) and angles (°) for **2b**

Zn(1)–O(1)	2.025(2)	Zn(1)–N(7)	2.048(3)
Zn(1)–O(18A)	2.123(3)	Zn(1)–C(35)	1.978(4)
Zn(2)–O(1)	2.117(3)	Zn(2)–N(12A)	2.027(3)
Zn(2)–O(18A)	2.032(2)	Zn(2)–C(37)	1.956(4)
O(1)–Zn(1)–N(7)	92.11(9)	O(1)–Zn(1)–O(18A)	85.49(9)
O(1)–Zn(1)–C(35)	116.02(15)	N(7)–Zn(1)–O(18A)	92.60(11)
N(7)–Zn(1)–C(35)	131.70(15)	O(18A)–Zn(1)–C(35)	126.05(16)
O(1)–Zn(2)–N(12A)	93.84(11)	O(1)–Zn(2)–O(18A)	85.48(9)
O(1)–Zn(2)–C(37)	123.76(19)	N(12A)–Zn(2)–O(18A)	93.07(10)
N(12A)–Zn(2)–C(37)	132.15(19)	O(18A)–Zn(2)–C(37)	116.12(16)
Zn(1)–O(1)–Zn(2)	93.89(9)	Zn(1)–O(18A)–Zn(2)	93.53(10)

the environment of the Zn_2O_2 ring has approximate C_2 symmetry about an axis perpendicular to the plane of the ring. The C_4 linkage between the two salicylaldimine moieties adopts an all *anti* conformation, the three C–C torsion angles being *ca.* −169, +174 and +178°. The C=N–C–C units, by contrast, have *gauche* conformations, being *ca.* −123 and +123°. This results in the O(1) and O(18) aryl rings at each end of the bis(salicylaldimine) ligand being inclined by only *ca.* 10°. A similar arrangement is seen for the closely related free ligand *N*,*N*′-bis(salicylidene)-1,4-butanediamine,[9] and for complexes of ligand **2a** with aluminium[10] and boron.[11] The structure of the gallium complex[12] of ligand **2a** has two independent molecules, one of which has the same *anti–anti–anti* conformation for the C–C bonds of the C_4 linkage as seen here in the structure of **2b**, whilst the other independent molecule has a *gauche–anti–gauche* conformation. All of these metal complexes are monomeric species, though polymers are known for a couple of silver complexes[13] and one manganese complex[14] of *N*,*N*′-bis(salicylidene)-1,4-butanediamine. These three polymeric species all have all *anti* conformations along the C_4 linkages. Adjacent repeat units within the polymer here in the structure of **2b** are related by a glide plane along the crystallographic *b* axis direction, and the $\{Zn_2O_2\}$ centroid···$\{Zn_2O_2\}$ centroid separation is *ca.* 10.4 Å.

^{1}H-NMR spectra of **1b–3b** reveal sharp quartet resonances for the methylene protons of the Zn-attached ethyl groups at 0.41, 0.40 and 0.43 ppm, respectively. The corresponding methyl resonances are obscured by the presence of several broadened resonances associated with the *t*-butyl groups of the phenoxy donors, the latter indicating that a fluxional process is operating, possibly involving monomer–oligomer equilibria in solution. Room temperature ^{13}C NMR spectra show the anticipated two pairs of resonances for the *t*-butyl substituents which are now sharp, a consequence of the longer relaxation time for the ^{13}C nuclei. The similar NMR features of **1–3** suggest closely related structures. However, there is a marked decrease in solubility in toluene and pentane as the spacer group is lengthened. A practical limit is reached at six methylene units beyond which the bimetallic zinc ethyl complexes can no longer be readily purified by re-crystallisation.

Bis-anilido–aldimine complexes

Next we targeted derivatives containing anilido–aldimine ligands. The ligands are comprised of two anilido–aldimine chelating centres separated by a flexible aliphatic spacer group whose length may be varied depending on the diamine employed. The fluorinated diimine compounds **4a** (n = 3) and **5a** (n = 6) were synthesised *via* the reation of two equivalents of

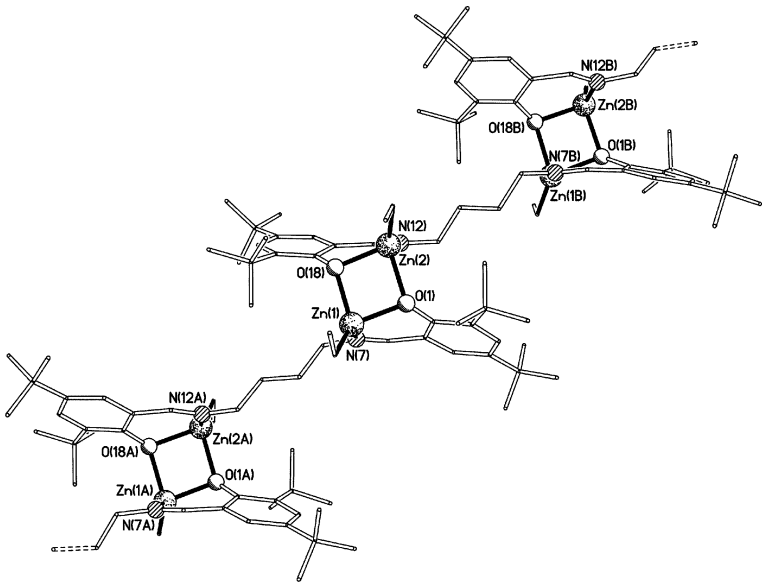
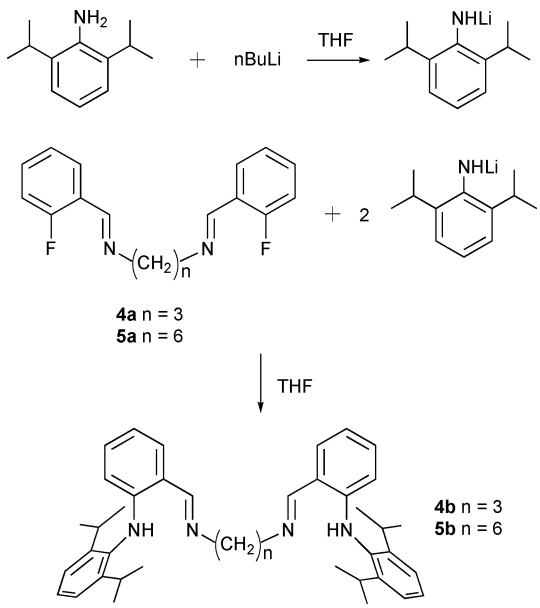


Fig. 2 Part of one of the extended chains present in the crystal of **2b**.

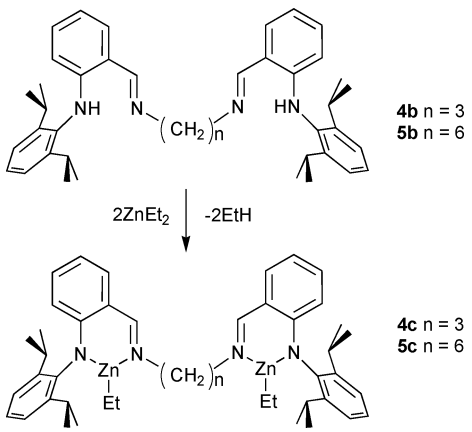
2-fluorobenzaldehyde with the appropriate diamine in hexane. The reaction of two equivalents of lithiated 2,6-diisopropylaniline with the resultant fluorinated diimines, followed by the addition of an extra equivalent of nBuLi yielded pro-ligands **4b** ($n = 3$) and **5b** ($n = 6$) after workup (Scheme 3).



Scheme 3 Synthesis of **4b** and **5b**.

Treatment of one equivalent of either **4b** or **5b** with two equivalents of diethyl zinc in toluene gave compounds **4c** and **5c**, respectively, as yellow crystalline solids (Scheme 4). **4c** and **5c** could be recrystallised from toluene–pentane (50 : 50) mixtures.

By contrast to the polymeric structure found for **2b**, the structure of **4c** is a bimetallic species. The zinc centres here are trigonal planar, the smallest angle at each corresponding to the bite of the N,N' chelate ligand (Table 2, Fig. 3).



Scheme 4 Synthesis of **4c** and **5c**.

The two six-membered C_3N_2Zn chelate rings have noticeably different conformations; that at Zn(1) has a folded geometry with the carbon and nitrogen atoms of the C=N(7) imine unit lying *ca.* 0.24 and 0.37 Å out of the {Zn(1),N(1),C(1),C(6)} plane (which is coplanar to within *ca.* 0.02 Å), whilst that at Zn(2) has a slight sofa conformation with the metal lying *ca.* 0.11 Å out of the $\{C_3N_2\}$ plane (which is coplanar to within *ca.* 0.02 Å). In contrast to the all *anti* conformation seen for the C_4 linkage between the two imine units in the structure of **2b**, here the C_3 linkage has a mixed conformation, the N(7)–C–C–C and C–C–C–N(11) torsion angles being *ca.* 60 (*gauche*) and 178° (*anti*) respectively. The C=N–C–C moieties have near orthogonal conformations, the torsion angles

Table 2 Selected bond lengths (Å) and angles (°) for **4c**

Zn(1)–N(1)	1.942(2)	Zn(1)–N(7)	1.984(2)
Zn(1)–C(42)	1.968(3)	Zn(2)–N(11)	2.001(2)
Zn(2)–N(17)	1.9307(19)	Zn(2)–C(44)	1.958(3)
N(1)–Zn(1)–N(7)	94.97(8)	N(1)–Zn(1)–C(42)	130.87(12)
N(7)–Zn(1)–C(42)	133.82(12)	N(11)–Zn(2)–N(17)	96.11(8)
N(11)–Zn(2)–C(44)	122.76(11)	N(17)–Zn(2)–C(44)	141.04(10)

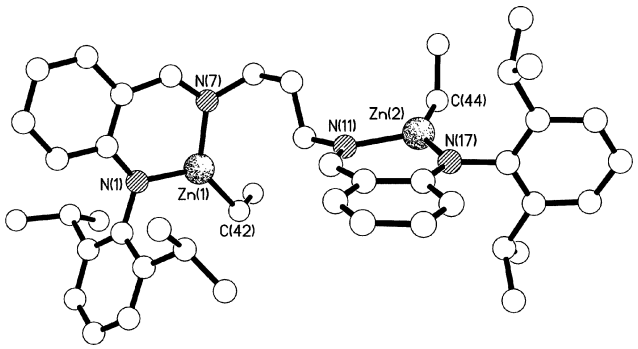


Fig. 3 The molecular structure of **4c**. The Zn(1)···Zn(2) separation is 6.3840(6) Å.

being *ca.* 95 and 102° for the N(7) and N(11) containing moieties respectively. As a result, the two anilido–aldimine aryl rings are oriented approximately orthogonally (inclined by *ca.* 79°) *cf.* the near co-planar arrangement in **2b** (inclined by *ca.* 10°). Similar *gauche–anti* conformations for the C_3 linkage are seen in the structures of the free ligand *N*,*N*′-bis(2-tosylaminobenzylidene)-1,3-propanediamine[15] and its zinc[16] and nickel[17] complexes. The crystal structure of **5c** shows similar features to **4c** with minimal differences between the Zn–O and Zn–N bond distances and angles. Further details for this structure are provided in the ESI.†

Conclusions

A successful synthetic strategy has been developed for the synthesis of bi- and multi-metallic complexes containing zinc centres separated by different length aliphatic spacer groups. In the case of salicylaldiminato derivatives, extended coordination polymers form *via* bis-chelation of the zinc centres, a consequence of the steric accessibility of the phenoxide oxygen donors for bridging between metals. The greater steric hindrance of anilido–aldimine ligands bearing the 2,6-diisopropylphenyl amide donor results in discrete dimeric products.

Experimental

General considerations

All reactions were carried out using standard Schlenk techniques unless otherwise stated. Toluene and pentane were dried by passing through a cylinder filled with commercially available Q-5 catalyst (13% Cu(II) oxide on Al_2O_3) and activated Al_2O_3 (3 mm, pellets) under a stream of nitrogen. All other solvents were distilled over standard drying agents under nitrogen. The solvents were degassed before use. All reagents were obtained from Aldrich Chemical Co. and used as received except for 2,6-diisopropylaniline which was purified by vacuum distillation prior to use. NMR spectra were recorded on Bruker 250 MHz, DRX-400 MHz or AM-500 MHz spectrometers. NMR chemical shifts are quoted in ppm relative to the residual protio solvent resonances.

Preparations

Synthesis of 1a. To a solution of 3,5-di-*t*-butyl salicylaldehyde (7.57 g, 0.032 mol) in ethanol was added 1,3-diaminopropane (1.35 cm^3, 0.016 mol). After several minutes, a bright yellow precipitate formed from the yellow solution. The mixture was allowed to stir for a further 2 h. The solid product was isolated by filtration and dried under vacuum. Yield: 84% (6.81 g). ^{1}H-NMR (298 K, $CDCl_3$, 250 MHz): δ 8.41 (2H, s, *H*C=N), 7.41 (2H, s, Ar), 7.10 (2H, s, Ar), 3.72 (4H, t, NCH_2), 2.14 (2H, quint, $CH_2CH_2CH_2$), 1.47 (18H, s, ^{t}Bu), 1.32 (18H, s, ^{t}Bu). ^{13}C-NMR ($CDCl_3$, 125.76 MHz): δ 169.32, 158.13, 140.06, 136.70, 126.89, 125.86, 35.07, 34.15, 31.74, 29.47. Elem. Anal. Cald. for $C_{33}H_{50}N_2O_2$: C, 78.21; H, 9.94; N, 5.53. Found: C, 78.12; H, 9.96; N, 5.59%.

Synthesis of 2a. An analogous procedure to that described for the synthesis of **1a** was employed, using 3,5-di-*t*-butyl salicylaldehyde (10.16 g, 0.043 mol) and 1,4-diaminobutane (1.91 g, 0.022 mol). The mixture was allowed to stir overnight before work-up. Yield: 79% (9.05 g). ^{1}H-NMR (298 K, $CDCl_3$, 250 MHz): δ 13.90 (2H, s, –O*H*), 8.38 (2H, s, –*H*C=N), 7.40 (2H, s, Ar), 7.09 (2H, s, Ar), 3.64 (4H, br, CH_2N), 1.82 (4H, br, CH_2CH$_2$N), 1.47 (18H, s, ^{t}Bu), 1.33 (18H, s, ^{t}Bu). ^{13}C-NMR (298 K, $CDCl_3$, 125.76 MHz): δ 165.97, 158.13, 139.95, 136.66, 126.79, 125.78, 117.83, 59.26, 35.03, 34.13, 31.52, 29.45, 28.56. Elem. Anal. Cald. for $C_{34}H_{52}N_2O_2$: C, 78.41; H, 10.06; N, 5.38. Found: C, 78.67; H, 10.15; N, 5.29%.

Synthesis of 3a. An analogous procedure to that described for the synthesis of **1a** was employed, using 3,5-di-*t*-butyl salicylaldehyde (8.00 g, 0.034 mol) and 1,6-diaminohexane (1.99 g, 0.017 mol). The mixture was allowed to stir overnight before work-up. Yield 72% (6.71 g). ^{1}H-NMR (298 K, $CDCl_3$, 250 MHz): δ 8.35 (2H, s, –C=N*H*), 7.38 (2H, s, Ar), 7.09 (2H, s, Ar), 3.58 (4H, t, CH_2N), 1.72 (4H, m, CH_2CH$_2$N), 1.46 (18H, s, ^{t}Bu), 1.45 (4H, m, CH_2CH$_2$CH$_2$N), 1.31 (18H, s, ^{t}Bu). ^{13}C-NMR (298 K, $CDCl_3$, 125.76 MHz): δ 165.61, 158.32, 139.77, 136.62, 126.65, 125.64, 117.79, 59.38, 35.01, 34.11, 31.50, 30.73, 29.43, 26.85. Elem. Anal. Cald. for $C_{36}H_{56}N_2O_2$: C, 78.78; H, 10.28; N, 5.10. Found: C, 78.98; H, 10.20; N, 5.06%.

Synthesis of 1b. To a solution of **1a** (3.53 g, 0.007 mol) in toluene (100 cm^3) was added $ZnEt_2$ (1.44 cm^3, 0.014 mol) at 0 °C. After warming the mixture to room temperature and stirring overnight, the resultant yellow precipitate was isolated by filtration and re-crystallised from toluene (20 cm^3). Yield 60% (2.91 g). ^{1}H-NMR (298 K, C_6D_6, 250 MHz): δ 7.72–7.36 (2H, m, –*H*C=N), 7.06–6.82 (4H, m, Ar), 3.52–2.66 (2H, m, CH_2CH$_2$N), 1.73–1.61 (18H, m, ^{t}Bu), 1.48–1.34 (18H, m, ^{t}Bu and 6H, m, ZnCH$_2$CH_3; overlapping resonances), 0.41 (4H, quintet, ZnCH_2CH$_3$). ^{13}C-NMR (298 K, CD_2Cl_2, 63 MHz): δ173.36, 171.48, 169.13, 166.40, 141.68, 137.81, 136.04, 130.67, 129.89, 129.49, 128.69, 125.78, 119.74, 117.51, 58.56, 35.97, 34.34, 31.81, 30.39, 39.86, 12.23 (ZnCH$_2$*C*H$_3$), 1.82 (*C*H$_2$CH$_3$). Elem. Anal. Cald. for $C_{37}H_{58}N_2O_2Zn_2$: C, 64.07; H, 8.43; N, 4.04. Found: C, 63.78; H, 8.67; N, 3.97%.

Synthesis of 2b. To a solution of **2a** (4.31 g, 0.0083 mol) in toluene (100 cm^3) was added $ZnEt_2$ (1.69 cm^3, 0.0166 mol) at 0 °C. After warming the mixture to room temperature and stirring overnight, the resultant yellow precipitate was isolated by filtration and re-crystallised from toluene (20 cm^3). Yield 57% (3.35 g). ^{1}H-NMR (298 K, C_6D_6, 400 MHz): δ 7.72 (2H, s, *H*C=N), 7.53 (2H, s, Ar), 6.90 (2H, s, Ar), 3.50–2.74 (4H, br, CH_2CH_2), 1.75–1.68 (18H, m, ^{t}Bu), 1.40–1.28 (18H, m, ^{t}Bu and 6H, m, ZnCH$_2$CH_3; overlapping resonances), 0.40 (4H, q, ZnCH_2CH$_3$). ^{13}C-NMR

(298 K, C_6D_6, 100.61 MHz): δ 172.02, 170.68, 141.51, 136.20, 129.88, 60.27, 59.62, 35.69, 33.83, 31.43, 29.72, 11.40, 2.52. Elem. Anal. Cald. for $C_{38}H_{60}N_2O_2Zn_2$: C, 64.49; H, 8.55; N, 3.96. Found: C, 64.53; H, 8.72; N, 3.85%.

Synthesis of 3b. To a solution of **3a** (4.31 g, 0.0083 mol) in toluene (100 cm^3) was added $ZnEt_2$ (1.69 cm^3, 0.0166 mol) at 0 °C. After warming the mixture to room temperature and stirring overnight, the resultant yellow precipitate was isolated by filtration and re-crystallised from toluene (30 cm^3). Yield 53% (0.74 g). ^{1}H-NMR (298 K, C_6D_6, 250 MHz): δ 7.76–7.67 (2 H, m, *H*C=N), 7.59 (2H, s, Ar), 6.93 (2H, s, Ar), 3.16–2.79 (4H, br, C*H*$_2$N) 1.39–1.35 (18H, m, ^{t}Bu and 6H, C*H*$_2$C*H*$_2$; overlapping resonances), 1.76–1.67 (18H, m, ^{t}Bu), 1.18–0.90 (6H, br, ZnCH$_2$C*H*$_3$) 0.43 (4H, q, ZnC*H*$_2$CH$_3$). ^{13}C-NMR (298 K, C_6D_6, 100.61 MHz): δ 170.55, 141.47, 136.23, 129.75, 60.74, 35.69, 33.77, 31.43, 29.72, 26.35, 11.42 (ZnCH$_2$*C*H$_3$), 2.33 (Zn*C*H$_2$CH$_3$). Elem. Anal. Cald. for $C_{40}H_{64}N_2O_2Zn_2$: C, 65.30; H, 8.77; N, 3.81. Found: C, 65.11; H, 8.75; N, 8.82%.

Synthesis of 4a. To a solution of 1,3-diaminopropane (2.98 g, 40 mmol) in hexane (30 cm^3) was added 2-fluorobenzaldehyde (10 g, 81 mmol). After stirring for 12 h, a quantity of water was seen to collect at the bottom of the reaction flask. The solution was dried over $MgSO_4$ and the product then re-crystallised from hexane by standing for one day at −25 °C, yielding white needle-like crystals. Yield 89% (10.2 g) ^{1}H NMR (298 K, $CDCl_3$, 400 MHz): δ 2.04 (2H, quintet, C*H*$_2$CH$_2$), 3.64 (4H, t, CH$_2$C*H*$_2$), 7.00–7.96 (8H, m, Ar), 8.50 (2H, s, N=C*H*). ^{13}C NMR (298 K, $CDCl_3$, 100.61 MHz): δ 31.91, 59.42, 115.66, 124.15, 127.65, 131.94, 154.18, 160.83, 163.33. Elem. Anal. Cald. for $C_{17}H_{16}F_2N_2$: C, 71.31; H, 5.63; N, 9.78. Found: C, 71.23; H, 5.74; N, 9.86%.

Synthesis of 5a. Using a procedure analogous to that described for **4a**, 2-fluorobenzaldehyde (20 g, 16 mmol) was added to a solution of 1,3-diaminohexane (9.36 g, 81 mmol) in hexane (30 cm^3). The product was isolated as white needle-like crystals. Yield 91% (24.2 g). ^{1}H NMR (298 K, $CDCl_3$, 400 MHz): δ 1.38 (4H, p, C*H*$_2$CH$_2$), 1.67 (4H, m, CH$_2$C*H*$_2$), 3.56 (4H, t, CH$_2$C*H*$_2$), 6.92–7.27 (6H, m, Ar), 7.93 (2H, m, Ar), 8.50 (2H, s, N=C*H*). ^{13}C NMR (298 K, $CDCl_3$, 100.61 MHz): δ 27.11, 30.79, 61.90, 115.66, 124.17, 127.64, 131.85, 153.70, 160.80, 163.31. Elem. Anal. Cald. for $C_{20}H_{22}F_2N_2$: C, 73.15; H, 6.75; N, 8.53. Found: C, 73.21; H, 6.90; N, 8.62%.

Synthesis of 4b. To a solution of 2,6-diisopropylaniline (24.38 cm^3, 140 mmol) in THF (100 cm^3) was added n-BuLi 2.5 M solution in hexane (56 cm^3, 140 mmol) while stirring at 0 °C. The solution was allowed to warm to room temperature and stirred for 12 h, after which the solution was light red in colour. This solution was added to a colourless solution of compound **4a** (20 g, 70 mmol) in THF (100 cm^3). The resultant dark orange solution was stirred overnight. An additional equivalent of BuLi was then added (28 cm^3, 70 mmol) at 0 °C. The solution darkened considerably and was left to stir for a further 12 h. Distilled water (200 cm^3) was then carefully added and the organic layer was separated and dried over $MgSO_4$. After removal of solvent under reduced pressure, the resultant residue was recrystallised from pentane to yield a cream-coloured crystalline solid. Yield 37% (31 g). ^{1}H NMR (298 K, $CDCl_3$, 400 MHz): δ 1.19 (24H, m, ^{i}Pr), 2.11 (2H, quintet, C*H*$_2$CH$_2$), 3.18 (4H, p, ^{i}Pr), 3.78 (4H, t, CH$_2$C*H*$_2$), 6.28 (2H, m, Ar), 6.69 (2H, m, Ar), 7.09–7.37 (10H, m, Ar), 8.47 (2H, s, N=C*H*), 10.62 (N*H*). ^{13}C NMR (298 K, $CDCl_3$, 100.61 MHz): δ −1.79, 11.89, 24.27, 27.87, 34.38, 58.82, 112.69, 113.73, 116.09, 123.72, 124.98, 133.83, 137.00, 143.53, 144.55, 157.34, 169.40. Elem. Anal. Cald. for $C_{41}H_{52}N_4$: C, 81.95; H, 8.72; N, 9.32. Found: C, 82.03; H, 8.72; N, 9.19%.

Synthesis of 5b. Using an analogous procedure to that described for the synthesis of **4b**, n-BuLi (2.5 M solution in hexane; 56 cm^3, 140 mmol) was added to a solution of 2,6-diisopropylaniline (27.3 cm^3, 140 mmol) in THF (100 cm^3) while stirring at 0 °C. The resultant light red coloured solution was added to a colourless solution of **5a** (22.99 g, 70 mmol) in THF (100 cm^3). Yield 27% (24.0 g). ^{1}H NMR (298 K, $CDCl_3$, 400 MHz): δ 1.17 (12H, m, ^{i}Pr), 1.18 (12H, m, ^{i}Pr), 1.45 (4H, m, C*H*$_2$CH$_2$), 1.71 (4H, m, NCH$_2$C*H*$_2$), 3.16 (4H, sept, ^{i}Pr), 3.63 (4H, t, NC*H*$_2$), 6.25 (2H, d, Ar), 6.69 (2H, t, Ar), 7.09–7.37 (8H, m, Ar), 8.46 (2H, s, N=C*H*), 10.65 (N*H*). ^{13}C NMR (298 K, $CDCl_3$, 100.61 MHz): δ 22.88, 24.93, 27.16, 28.49, 31.36, 61.47, 111.62, 114.90, 116.75, 123.70, 127.16, 130.88, 133.38, 135.30, 147.54, 149.43, 164.04. Elem. Anal. Cald. for $C_{44}H_{58}N_4$: C, 82.19; H, 9.09; N, 8.71. Found: C, 80.85; H, 8.66; N, 8.52%.

Synthesis of 4c. To a solution of compound **4b** (2.45 g, 4.08 mmol) in toluene–pentane (50 : 50, 100 cm^3) at 0 °C was added $ZnEt_2$ (1.00 g, 8.15 mmol). The colourless solution immediately became bright yellow and was stirred for a further 12 h at room temperature. The solution was concentrated under reduced pressure and left to stand at −25 °C for 12 h after which yellow crystals of **4c** had formed. Yield 57% (1.83 g). ^{1}H NMR (298K, $CDCl_3$, 400 MHz): δ 0.25 (4H, q, ZnC*H*$_2$CH$_3$), 0.91 (6H, t, ZnCH$_2$C*H*$_3$), 1.12 (12H, d, ^{i}Pr), 1.20 (12H, d, ^{i}Pr), 2.30 (2H, p, C*H*$_2$CH$_2$), 3.08 (4H, septet, ^{i}Pr), 3.88 (4H, t, CH$_2$C*H*$_2$), 6.32 (6H, m, Ar), 7.93 (2H, m, Ar), 8.50 (2H, s, N=C*H*). ^{13}C NMR (298 K, $CDCl_3$, 100.61 MHz): δ −1.79, 11.89, 24.27, 27.87, 34.38, 58.82, 112.69, 113.73, 116.09, 123.72, 124.98, 133.83, 137.00, 143.53, 144.55, 157.34, 169.40. Elem. Anal. Cald. for $C_{45}H_{60}N_4Zn_2$: C, 68.61; H, 7.68; N, 7.11. Found: C, 68.56; H, 7.81; N, 7.09%.

Synthesis of 5c. Using an analogous procedure to that described for the synthesis of **4c**, $ZnEt_2$ (1.10 g, 8.93 mmol) was added to a solution of **5b** (2.87 g, 4.46 mmol) in toluene (100 cm^3) at 0 °C. The product **5c** was isolated as yellow crystals. Yield 52% (1.92 g). ^{1}H NMR (298 K, $CDCl_3$, 400 MHz): δ 0.26 (4H, q, ZnC*H*$_2$CH$_3$), 0.98 (6H, t, ZnCH$_2$C*H*$_3$), 1.14 (12H, d, ^{i}Pr), 1.22 (12H, d, ^{i}Pr), 1.53 (4H, m, C*H*$_2$CH$_2$), 1.87 (4H, m, C*H*$_2$CH$_2$), 3.08 (4H, septet, ^{i}Pr), 3.81 (4H, t, CH$_2$C*H*$_2$), 6.31 (2H, d, Ar), 6.50 (2H, t, Ar), 7.08–7.31 (10H, m, Ar), 8.41 (2H, s, N=C*H*). ^{13}C NMR (298 K, CD_2Cl_2, 100.61 MHz), 100.62 MHz): δ −1.57, 12.23, 24.51, 27.10, 28.27. 32.53, 61.91, 112.81, 114.60, 116.17, 124.10, 125.26, 133.84, 137.48, 144.10, 145.34, 157.49, 169.44. Elem. Anal. Cald. for $C_{48}H_{66}N_4Zn_2$: C, 69.47; H, 8.02; N, 6.75 Found: C, 69.59; H, 8.13; N, 6.72%.

X-Ray crystallography

Crystal data for 2b. $C_{38}H_{60}N_2O_2Zn_2$, $M = 707.62$, orthorhombic, *Aba*2 (no. 41), $a = 18.1320(8)$, $b = 18.8215(7)$, $c = 23.1100(9)$ Å, $V = 7886.8(54)$ Å^3, $Z = 8$, $D_c = 1.192$ g cm^{-3}, μ(Mo-Kα) = 1.248 mm^{-1}, $T = 173$ K, 12497 independent measured reflections, $R1 = 0.063$, $wR2 = 0.149$.

Crystal data for 4c. $C_{45}H_{60}N_4Zn_2$, $M = 787.71$, triclinic, $P\bar{1}$ (no. 2), $a = 8.9147(5)$, $b = 14.7627(9)$, $c = 16.4967(9)$ Å, $\alpha = 88.863(6)$, $\beta = 86.406(4)$, $\gamma = 72.948(5)°$, $V = 2071.5(2)$ Å^3, $Z = 2$, $D_c = 1.263$ g cm^{-3}, μ(Cu-Kα) = 1.676 mm^{-1}, $T = 173$ K, 7684 independent measured reflections, $R1 = 0.042$, $wR2 = 0.120$.

Crystal data for 5c. $C_{48}H_{66}N_4Zn_2$, $M = 829.79$, monoclinic, $P2_1/n$ (no. 14), $a = 11.5694(6)$, $b = 13.4841(8)$, $c = 14.3159(7)$ Å, $\beta = 98.626(4)°$, $V = 2208.1(2)$ Å^3, $Z = 2$, $D_c = 1.248$ g cm^{-3}, μ(Mo-Kα) = 1.122 mm^{-1}, $T = 173$ K, 7658 independent measured reflections, $R1 = 0.045$, $wR2 = 0.095$.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615080b

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