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Synthesis and structural diversity of 2-pyridylmethylideneamine complexes of zinc(II) chloride

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ABSTRACT

The addition reactions of zinc(II) chloride to *N*-substituted pyridine-2-carbaldimines [Py-CH=NR, R = Me (1a), Ph (1b), Bz (1c), allyl (1d)] lead to different complexes dependent on the *N*-bound substituent R. The 1:1 complexes show molecular structures of the type [(Py-CH=NR)ZnCl₂] for R = methyl (2a), phenyl (2b), and allyl (2d) with a distorted tetrahedral environment for the zinc atom. The zinc complex with the *N*-methylated pyridine-2-carbaldimine also forms a dimer of the type [(Py-CH=NR)ZnCl₂]₂ (2a)₂ with a square pyramidal coordination sphere of zinc. A 3:2 stoichiometry is observed for R = benzyl and an ion pair of the type [Zn(Py-CH=NR)]²⁺ [ZnCl₄]²⁻ (2c) is found in the solid state.

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1. Introduction

Our ongoing research focuses on the synthesis of oligodentate ligands for dinuclear complexes with a 1,2-di(2-pyridyl)ethane backbone such as substituted 1,2-dipyridyl-1,2-diaminoethanes. Thus, the bis(alkylzinc) substituted derivatives A (Scheme 1) of these tetra-dentate azaligands are accessible *via* an oxidative C–C coupling reaction of 2-pyridylmethylamines with excess of dialkylzinc at elevated temperatures [1,2]. Similar dinuclear zinc complexes with the *N*,*N*'-di(*tert*-butyl)-1,2-di(2-pyridyl)-1,2-diamidoethane ligand were prepared by van Koten and coworkers [3-6]. Protonation of these complexes with acetamide yields N,N'-substituted 1,2-dipyridyl-1,2-diaminoethanes B [7] which are also accessible via a reductive coupling of 2-pyridylmethylideneamines 1 [8-10]. The 2-pyridylmethylidene-amines 1 (azomethines) are easily accessible by straight-forward procedures and therefore represent convenient starting materials for the synthesis of these ligands. Despite the availability of these imines, there exist only very few zinc(II) chloride complexes of these ligands (2a [11], 2b [12]) which were, however, not characterized by X-ray structure analysis (Scheme 2). In order to investigate the reductive coupling of these imines in the boundary of a zinc(II) ion, we were interested in the coordination behaviour of these imines. The applied azomethines 1 are wellknown and in some cases even commercially available [R = methyl (Me) [11], phenyl (Ph), benzyl (Bz), allyl [13]].

2. Results and discussion

The azomethines **1a–d** were prepared by stirring of pyridine-2carboxyaldehyde and the corresponding amine in methylene chloride or water. All azomethines were obtained with moderate to excellent yields as shown in Table 1. The zinc(II) chloride complexes **2** of these azomethines **1** were prepared by adding a solution of azomethine in anhydrous methanol to a stirred solution of the metal salt (see Table 1). All compounds described in this paper are fully characterized by ¹H, ¹³C, DEPT135, HSQC, HMBC NMR, IR, mass spectrometry, elemental analysis, and single crystal X-ray diffraction experiments.

Zinc atoms favor tetrahedral environments, however, depending on the bulkiness of the ligands coordination numbers between two and six can be realized. Here we show that tetrahedral, square pyramidal and octahedral coordination spheres are observed depending solely on the N2-bound substituent. The crystalline state of complex 2a (see Figs. 1 and 2) contains dimeric and monomeric complexes at the same time in a 1:1 ratio ("A" and "B" distinguish between the mono- and dinuclear complex, in molecule B "a" is used for equivalent atoms generated by symmetry transformation -x + 1, -y + 1, -z + 2). In the dimer the zinc atom is in a square pyramidal environment with the basis formed by the azomethine moiety and two bridging chloro ligands whereas another chloro ligand occupies the apical position. The monomeric zinc complex contains a distorted tetrahedrally coordinated zinc atom. For N2 a nearly planar surrounding is found in both species (angle sums 359.9°) and due to the small bites of the ligands narrow N1–Zn–N2 angles $(80.66(9)^{\circ}$ in the monomer and $77.33(9)^{\circ}$ in





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R = Alkyl, Aryl; M = Zn/Me₃SiCl, Mg/Me₃SiCl, Al, Bi

Scheme 1. Oxidative C–C coupling reaction and protolysis of the thus formed zinc complex (upper pathway) and reductive C–C coupling (lower pathway).

the dimer) are observed. Regarding the Zn–Cl bond lengths in both species significant differences are found. The smaller coordination number of the zinc atoms leads to shorter Zn–Cl bonds. Furthermore the Zn–Cl distance of the terminal chloro ligand in the dimer lies within the expected range [14] (224.04(8) pm) whereas two significantly different Zn–Cl distances are observed for the μ -chloro ligands (239.85(7) and 250.99(9) pm). Selected bond



Scheme 2. Reaction scheme for the formation of the zinc complexes 2a-d.

Table 1Yields of the imines 1 and their zinc(II) complexes 2.

1, 2	R	Yield of 1 (%)	Yield of 2 (%)
a	Me	84	87
b	Ph	85	83
с	Bz	94	85
d	allyl	65	90
a b c d	Ph Bz allyl	84 85 94 65	87 83 85 90



Fig. 1. Molecular structure and numbering scheme of **2a**. The ellipsoids represent a probability of 40%, H atoms are shown with arbitrary radii. The letter "a" is used for equivalent atoms generated by symmetry transformation -x + 1, -y + 1, -z + 2.

lengths and angles are summarized in Table 2. Fragments of the dimer of **2a** were detected in a FAB mass spectrum such as the $[(2a)_2-Cl]^+$ ion at m/z = 477 with a low intensity. Comparison of the experimental isotopic pattern with the calculated one confirmed this interpretation (Fig. 3). Despite these results which show that monomeric and dimeric **2a** are present in the solid and the gaseous phase, only one set of signals was observed in the solution by NMR spectroscopy. Either the influence of the aggregation on the chemical shift of the ligand's atoms is too small for discrimination between the two coordination spheres or the monomer/dimer equilibrium is fast on the NMR time scale.

Replacement of the methyl group by a phenyl substituent leads to the monomeric zinc complex **2b** with a distorted tetrahedral environment of the zinc atom (see Fig. 4). Due to the small bite of the ligand the N1–Zn–N2 angle shows a value of only 80.8(3)°. The Zn–N and Zn–Cl bond lengths lie in characteristic regions [14]. N2 exhibits a planar environment with an angle sum of 360.0°. Both aryl rings are arranged coplanarily.

A different structure is realized in the case of R = benzyl (**2c**). In this dinuclear zinc complex, which crystallizes in the space group $P2_1/n$, an ion pair is observed. In the cation the zinc atom is in a distorted octahedral coordination sphere, the counter anion being the well-known $[ZnCl_4]^{2-}$ anion (Fig. 5, the three ligands of the cation are distinguished by the letters "A", "B", and "C"). Due to the crystallographic inversion symmetry a racemate of the Δ - and Λ isomers is found in the solid state. In the gaps between the ions two host methanol molecules per asymmetric unit of **2c** are



Fig. 2. Part of the crystal structure of 2a showing the packing of the mono- and dinuclear molecules in the solid state.

I dDIE Z	Table	2
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Comparison of selected bond lengths [pm] and angles [°].

Parameter	2a A	2a B	2b	2c	2d
Zn–N1	206.2(2)	212.6(2)	206.3(8)	220.4 ^a	206.73(14)
Zn-N2	206.1(2)	214.2(3)	208.5(8)	216.8 ^a	206.46(14)
Zn-Cl1 (terminal)	220.98(8)		222.6(3)	225.28(10)	220.56(4)
Zn-Cl2 (terminal)	221.23(8)	224.04(8)	220.0(3)	228.83(9)	222.13(5)
Zn-Cl3 (terminal)				227.12(10)	
Zn-Cl4 (terminal)				228.79(9)	
Zn–Cl1 (bridging)		239.85(7)			
Zn-Cl1a (bridging)		250.99(9)			
N2-C6	127.5(4)	128.0(4)	125.5(12)	127.6 ^a	126.9(2)
N2-C7	146.6(4)	146.5(4)	145.1(12)	146.7 ^a	146.7(2)
C6–C5	147.4(4)	147.4(4)	149.0(13)	147.7 ^a	146.9(3)
N1–Zn–N2	80.66(9)	77.33(9)	80.8(3)	76.47 ^a	80.99(6)
Cl–Zn–Cl (tetrahedral)	115.06(3)		115.90(18)		115.190(18)

^a Average values.

intercalated as also found in the elemental analysis. The small N1– Zn–N2 angle (averaged 76.47°) leads to distortion from octahedral geometry. Again, N2 is in a planar environment with an angle sum of 359.9°. The coordination number of the metal ion strongly influences the Zn–N bond lengths and the Zn–N distances of the cation with a six-coordinate zinc atom are larger than those in the complexes with tetrahedrally or square pyramidically coordinated metal atoms (see Table 2). Furthermore the planes of the phenyl ring (e.g. ligand B) are roughly coplanar to the N1–C5–C6–N2–Zn plane of the neighbor ligand (e.g. of ligand C) with an average distance of approximately 335 pm. This rather small distance (comparable to the distance of the layers in graphite) allows a π - π interaction between the N1–C5–C6–N2 moieties and the phenyl rings thus allowing and stabilizing the large coordination number of the zinc atom.

Reduction of the ability to form π -stacking structures leads to conventional structures with tetra-coordinate zinc atoms as found for the derivative with R = allyl (**2d**) (Fig. 6). As expected the small bite of the ligand leads again to a narrow N1–Zn–N2 angle of 80.99(6)° which also is the reason for the distorted geometry. The atom N2 exhibits a planar environment with an angle sum of 359.4°. In addition, the Zn–Cl and Zn–N as well as the C–C bond



Fig. 3. Comparison of the fragment $[(2a)_2-Cl]^+$ with the calculated isotopic pattern. The upper spectrum shows the experimental data while the lower represents the calculated values. The spectra show m/z in relation to relative intensities [%].



Fig. 4. Molecular structure and numbering scheme of **2b**. The ellipsoids represent a probability of 40%; H atoms are shown with arbitrary radii.



Fig. 5. Molecular structure and numbering scheme of **2c**. The ellipsoids represent a probability of 40%; H atoms and methanol solvent molecules have been omitted for clarity.



Fig. 6. Molecular structure and numbering scheme of 2d. The ellipsoids represent a probability of 40%, H atoms are shown with arbitrary radii.

Table 3

Comparison of the Cl–Zn–Cl angle [°] with the Zn–Cl and Zn–N bond lengths [pm] of presented and selected published compounds of the type $(L_2)ZnCl_2$.

Compound	ClZnCl (°)	Zn-Cl (pm)	Zn–N (pm)	Reference
[{H ₂ N(CH ₂) ₃ NMe ₂ }ZnCl ₂]	112.6	223.4	203.6	[21]
[(Py-CH=N-Me)ZnCl ₂]	115.1	221.1	206.2	
[(Py-CH=N-All)ZnCl ₂]	115.2	221.3	206.6	
[(Py-CH ₂ -N=CMe ₂)ZnCl ₂]	115.5	220.5	205.2	[17]
[(Py-CH=N-Ph)ZnCl ₂]	115.9	221.3	207.4	
[(bpy)ZnCl ₂]	117.1	220.4	205.9	[22]
[(Py-CH ₂ -N=CPh ₂)ZnCl ₂]	117.4	221.3	205.5	[20]
[(tmeda)ZnCl ₂]	119.0	221.4	209.2	[23]



Scheme 3. Numbering scheme of the pyridyl moiety for the assignment of the NMR parameters.

lengths lie well within expected ranges [14] and are comparable with those of the tetrahedral complexes **2a** and **2c**.

3. Conclusions

2-Pvridvlmethvlideneamines are not only suitable synthons in reductive C-C coupling reactions for the synthesis of 1.2-dipyridvl-1.2-diaminoethanes but also show an interesting coordination behaviour. N-organyl-pyridylmethylideneamines L stabilize coordination numbers of four, five and six at the zinc atom thus showing a strong influence of the coordination number on the nature of the organyl group. Methyl, phenyl, and allyl substituents lead to complexes of the type $[(L)ZnCl_2]$ with tetra-coordinate zinc atoms. For *N*-methyl-pyridylmethylideneamines also a dimeric complex of the type $[(L)(Cl)Zn(\mu-Cl)_2Zn(Cl)(L)]$ is observed in the crystalline state. The Zn₂Cl₂ ring shows significantly different Zn–Cl distances which suggest the formation of a loose dimer. However, even in the gaseous phase, fragments stemming from the dimer are found. Zinc complexes with N-benzyl-pyridylmethylideneamine ligands are stabilized by π -stacking of the aryl groups allowing a coordination number of six for the metal atom. This behaviour leads to the formation of the dinuclear ion pair of the type $[(L)_3 Zn]^{2+} [ZnCl_4]^{2-}$.

The significantly different molecular structures are solely a consequence of the nature of the N-bound group. In addition the Cl-Zn-Cl angle in complexes with tetra-coordinate metal atoms strongly depends on the Zn-N distances to the neutral aza-coligands. Very weak Lewis bases lead to large X-Zn-X angles whereas strong donor ligands form complexes with a nearly tetrahedral environment of the zinc atom. Investigations on 2-pyridylmethylamine complexes of the zinc(II) halides already showed that ZnCl₂ forms a 1:1 adduct of the type [(L)ZnX₂] whereas the bromide and iodide yield ion pairs of the type $[(L)_2 ZnX]^+ X^-$ with penta-coordinate zinc atoms. A comparison of the mononuclear 2-pyridylmethylideneamine complexes of ZnCl₂ 2a, 2b, and 2d with e.g. (bpy)ZnCl₂, (tmeda)ZnCl₂ and (1-amino-3-dimethylaminopropane)zinc(II) chloride shows comparable structural parameters (Table 3). Not only that the donor strength of the amine proofed to be of importance but also the steric strain induced by the ligands

Table 4

Crystal data and refinement details for the X-ray structure determinations of the zinc complexes 2a-d.

Compound	2a	2b	2c	2d
Formula	C ₇ H ₈ Cl ₂ N ₂ Zn	$C_{12}H_{10}Cl_2N_2Zn$	[C ₃₉ H ₃₆ N ₆ Zn][Cl ₄ Zn]·CH ₄ O	C ₉ H ₁₀ Cl ₂ N ₂ Zn
Formula weight (g mol ⁻¹)	256.42	318.49	893.32	282.46
T (°C)	-90(2)	-90(2)	-90(2)	-90(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	ΡĪ	ΡĪ	$P2_1/n$	$P2_1/c$
a (Å)	7.7548(4)	7.7717(10)	11.8290(3)	8.8658(3)
b (Å)	8.6595(5)	8.6704(11)	15.4236(4)	16.8806(6)
c (Å)	14.6503(5)	9.8213(11)	21.6408(5)	7.8929(2)
α (°)	77.422(3)	100.901(7)	90.00	90.00
β (°)	83.897(3)	101.139(7)	94.651(2)	102.171(2)
γ (°)	79.259(3)	97.063(7)	90.00	90.00
V (Å ³)	941.15(8)	628.81(13)	3935.27(17)	1154.70(6)
Ζ	4	2	4	4
$\rho (\text{g cm}^{-3})$	1.810	1.682	1.508	1.625
μ (cm ⁻¹)	31.2	23.53	15.31	25.51
Measured data	6681	4198	27 832	7719
Data with $I > 2\sigma(I)$	3235	1801	5809	2316
Unique data/R _{int}	4273/0.0289	2761/0.0541	9017/0.0694	2619/0.0279
wR_2 (all data, on F^2) ^a	0.0799	0.2576	0.1105	0.0673
$R_1 (I > 2\sigma(I))^{\rm a}$	0.0343	0.0934	0.0446	0.0256
s ^b	0.954	1.082	0.993	1.029
Residence density (e Å ⁻³)	0.386/-0.563	1.129/-0.805	0.695/-0.696	0.265/-0.499
Absorption method	none	none	none	none
CCDC Number	717944	717945	717946	717947

^a Definition of the *R* indices: $R_1 = (\sum ||F_0| - F_c||) / \sum |F_0|$, $wR_2 = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2 (F_0^2) + (aP)^2$.

^b $s = \{\sum [w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}.$

as well as coligands. This correlation is not only valid for the halides but in general for all compounds of the type $[(L_2)ZnX_2]$ with X being halide or pseudohalide $([1,2-(bis-cinnamaldimino)-phenylZn(CN)_2]$: X–Zn–X = 113.6°; Zn–X = 200.5 pm; Zn–N = 205.0 pm [15]; $[{H_2N(CH_2)_2NEt_2}]Zn(NCS)_2]$: X–Zn–X = 111.9°; Zn–X = 192.9 pm; Zn–N = 204.8 pm [16]), or alkyl groups. If the donor base is very weakly bound at the zinc atom (most commonly induced by intramolecular steric strain) the coordination number of the zinc atom is reduced to three and multidentate coligands can act as monodentate ones. Correlations between the X–Zn–X angle and the Zn–N bond lengths have been published previously [17–19]. Bond angles and lengths presented in Table 3 also support these findings [17,20]. However, deviations can result from steric strain.

4. Experimental

4.1. General

All manipulations were carried out in an argon atmosphere under anaerobic conditions. Prior to use, all solvents were thoroughly dried and distilled in an argon atmosphere. Most of the compounds are moisture sensitive. ¹H and ¹³C NMR spectra were recorded at ambient temperature on a Bruker AC200 or a Bruker AC400 spectrometer. Assignment of the chemical shifts is shown in Scheme 3. Mass spectra were obtained on a Finnigan MAT SSQ 710 system or a Finnigan MAZ95XL, IR measurements were carried out on a Perkin–Elmer System 2000 FT-IR. Melting points were measured with a Reichert-Jung apparatus Type 302102 and are uncorrected. Peaks in the mass spectra were assigned by comparison of the observed isotopic patterns with the calculated ones. Starting azomethines **1a–d** were prepared according to literature procedures [24,25].

4.2. N-Methyl-pyridylmethylideneamine 1a

Pyridine-2-carbaldehyde (10.71 g, 0.10 mol) was dissolved in 10.0 ml of a 40% aqueous methylamine solution (0.13 mol methylamine) at 0 °C. After stirring for 1 h the mixture was extracted four times with 20 ml of methylene chloride each. The combined extracts were dried over anhydrous magnesium sulfate. Subsequently, the solvent was removed in vacuo and the obtained dark yellow oil was purified by vacuum distillation (53 °C at 1 mbar) giving 9.61 g of a pale yellow liquid. Yield: 83%; IR (KBr): *v* [cm⁻¹] = 3054 w, 3008 w, 2944 m, 2884 m, 2862 2773 w, 1652 st (C=N), 1586 st, 1567 st, 1470 st, 1454 m, 1437 st, 1401 w, 1347 m, 1291 w, 1221 w, 1147 w, 1124 w, 1044 w, 1006 m, 989 st, 969 w, 947 w, 862 w, 773 st, 742 m, 661 w, 617 m, 510 m; ¹H NMR (D₂O): *δ* = 8.34-8.30 (m, 1H, Pyr1), 8.05–8.03 (m, 1H, HC=N), 7.69 (ddd, 1H, Pyr3, J = 1.8 Hz, J = 7.6 Hz), 7.56–7.51 (m, 1H, Pyr4), 7.27 (dddd, 1H, Pyr2, J = 1.2 Hz, J = 7.4 Hz), 3.28 (d, 3H, CH₃, 1.6 Hz); 13 C NMR (D₂O): δ = 163.1 (t, C=N), 151.8 (q, Pyr5), 148.3 (t, Pyr1), 137.7 (t, Pyr3), 125.4 (t, Pyr2), 121.1 (t, Pyr4), 46.1 (p, CH₃); MS (EI): m/z (%) = 153 (17), 149 (7), 136 (16), 120 (25) [M]⁺, 119 (100), 105 (21), 92 (39), 78 (11), 77 (54), 52 (18), 51 (27), 39 (10), 28 (20); Elemental Anal. Calc. for (C₇H₈N₂, 120.152): C, 69.97; H, 6.71; N, 23.32. Found: C, 69.75; H, 6.76; N, 23.28%.

4.3. General procedure for the preparation of N-organylpyridylmethylideneamines **1b**–**d**

The amine (0.04 mol) was dissolved in 10 ml of methylene chloride and cooled to 0 °C. Pyridine-2-carbaldehyde (4.28 g, 0.04 mol) was added dropwise and the mixture was stirred for three hours at 0 °C. The solvent was removed in vacuo and the resulting products were purified by distillation.

4.4. N-Phenyl-pyridylmethylideneamine 1b

Yellow viscous oil (112 °C at $5 \cdot 10^{-3}$ mbar; solid beneath r.t.). Yield: 85%; IR (KBr): $v [cm^{-1}] = 3409$ w, 3053 m, 3015 m, 2906 w, 2893 w, 1623 st (C=N), 1579 st, 1563 st, 1487 st, 1466 st, 1451 m, 1433 st, 1347 m, 1197 m, 1147 m, 1074 m, 1045 m, 991 st, 980 m, 912 m, 877 m, 782 st, 740 st, 689 st, 665 m, 619 m, 552 m, 539 st; ¹H NMR (CD₂Cl₂): δ = 8.70 (d, 1H, Pyr1, J = 4.4 Hz), 8.60 (s, 1H, C=N), 8.22 (d, 1H, Pyr4, J = 8.0 Hz), 7.83 (ddd, 1H, Pyr3, J = 1.2 Hz, J = 7.6 Hz), 7.45–7.41 (m, 2H, m-PhH,), 7.38 (dddd, 1H, Pyr2, J = 1.2 Hz, J = 76 Hz), 7.30–7.27 (m, 3H, o,p-PhH); ¹³C NMR (CD₂Cl₂): δ = 161.4 (t, C=N), 155.2 (q, Pyr5), 151.5 (q, PhC), 150.0 (t, Pyr1), 136.9 (t, Pyr3), 129.6 (t, m-PhC), 127.0 (t, p-PhC), 125.5 (t, Pyr2), 121.7 (t, Pyr4), 121.4 (t, o-PhC); MS (DEI): m/z (%) = 211 (2), 182 (100) [M]⁺, 180 (53), 156 (14), 154 (11), 129 (3), 127 (7), 105 (28), 104 (32), 91 (23), 79 (24), 78 (28), 77 (81), 76 (28), 64 (3), 51 (28), 50 (19), 38 (8), 26 (15); Elemental Anal. Calc. for (C₁₂H₁₀N₂, 182.221): C, 79.10; H, 5.53; N, 15.37. Found: C, 79.10; H, 5.61; N, 15.33%.

4.5. N-Benzyl-pyridylmethylideneamine 1c

Pale yellow oil (121 °C at $7 \cdot 10^{-3}$ mbar; solid beneath r.t.). Yield: 94%; IR (KBr): ν [cm⁻¹] = 3275 w, 3058 m, 3028 m, 2880 m, 1647 st (C=N), 1586 st, 1567 st, 1495 m, 1467 st, 1451 st, 1434 st, 1378 m, 1335 m, 1225 w, 1144 w, 1077 w, 1043 m, 1028 m, 991 m, 861 w, 770 st, 737 st, 698 st, 616 m, 501 m; ¹H NMR (CD₂Cl₂): δ = 8.66 (d, 1H, Pyr1, *J* = 4.4 Hz), 8.53 (s, 1H, HC=N), 8.09 (d, 1H, Pyr4, *J* = 8.0 Hz), 7.75 (ddd, 1H, Pyr3, *J* = 1.6 Hz, *J* = 7.6 Hz), 7.40–7.38 (m, 4H, *o*,*m*-PhH), 7.33–7.30 (m, 2H, Pyr2/*p*-PhH), 4.88 (s, 2H, CH₂); ¹³C NMR (CD₂Cl₂): δ = 163.3 (t, C=N), 155.2 (q, Pyr5), 149.7 (t, Pyr1), 139.6 (q, PhC), 136.7 (t, Pyr3), 128.8 (t, *m*-PhC), 128.5 (t, *o*-PhC), 127.4 (t, *p*-PhC), 125.1 (t, Pyr2), 121.2 (t, Pyr4), 65.2 (s, CH₂); MS (DEI): *m/z* (%) = 196 (65) [M]⁺, 180 (98), 168 (29), 119 (91), 91 (100), 65 (64), 51 (34), 39 (18), 28 (6); Elemental *Anal.* Calc. for (C₁₃H₁₂N₂, 196.248): C, 79.29; H, 6.16; N, 14.27. Found: C, 79.29; H, 6.18; N, 14.40%.

4.6. N-Allyl-pyridylmethylideneamine 1d

Additionally anhydrous Na₂SO₄ was added to the reaction mixture and removed after completion of the reaction. Yellow liquid $(112 \circ C \text{ at } 5 \cdot 10^{-3} \text{ mbar})$, Yield: 65%; IR (KBr): $v [cm^{-1}] = 3055 \text{ m}$, 3012 m, 2982 w, 2884 m, 2821 m, 1650 st (C=N), 1586 st, 1567 st, 1468 st, 1436 st, 1418 w, 1356 w, 1314 m, 1291 w, 1226 w, 1146 w, 1106 w, 1087 w, 1044 m, 1023 m, 992 st, 920 st, 853w, 773 st, 742 m, 665 w, 632 w, 614 m, 560 w, 505 w; ¹H NMR $(CD_2Cl_2): \delta = 8.61$ (d, 1H, Pyr1, J = 4.4 Hz), 8.37 (s, 1H, HC=N), 8.03 (d, 1H, Pyr4, J = 8.0 Hz), 7.74 (ddd, 1H, Pyr3, J = 1.6 Hz, J = 7.6 Hz), 7.33–7.30 (m, 1H, Pyr2), 6.13–6.03 (m, 1H, HC=C), 5.32-5.14 (m, 2H, C=CH₂), 4.30-4.28 (m, 2H, CH₂); ¹³C NMR (CD₂Cl₂): δ = 163.3 (t, C=N), 155.2 (q, Pyr5), 149.7 (t, Pyr1), 136.7 (t, Pyr3), 136.2 (t, HC=C), 125.0 (t, Pyr2), 121.1 (t, Pyr4), 116.2 (s, C=CH₂), 63.6 (s, CH₂); MS (EI): m/z (%) = 147 (100) [M+1]⁺ 130 (94), 118 (10), 92 (6), 78 (8), 39 (15), 27 (14); Elemental Anal. Calc. for (C₉H₁₀N₂, 146.189): C, 73.94; H, 6.89; N, 19.16. Found: C, 74.13; H, 6.74; N, 19.35%.

4.7. [(N-Methyl-pyridylmethylideneamino) $ZnCl_2$]_n **2a** (n = 1, 2)

Anhydrous zinc(II) chloride (0.68 g, 5.0 mmol) was dissolved in 5 ml of anhydrous THF. The solution was cooled to 0 °C and the solution of **1a** (0.60 g, 5.0 mmol) in 2 ml anhydrous THF was added

dropwise, while immediately a colorless precipitate was formed. The suspension was diluted with additional 15 ml of anhydrous THF and stirred for half an hour. Subsequently the colorless precipitate was filtered off, washed with anhydrous THF and dried in vacuo, yielding 1.12 g of **2a**. Colourless needles, suitable for single crystal X-ray diffraction were obtained by cooling a saturated solution of 2a in acetone (r.t.) to 5 °C. Yield: 87%; m.p. 201 °C (dec.); IR (Nujol): $v [cm^{-1}] = 3104 w$, 3076 w, 3032 m, 1651 m, 1600 st, 1570 w, 1480 m, 1446 st, 1312 st, 1273 w, 1223 m, 1161 m, 1099 w, 1055 w, 1029 m, 1022 st, 975 m, 960 m, 873 w, 774 st, 746 w, 722 w, 668 w, 643 w, 508 m; ¹H NMR (CD₃OD): δ = 8.71 (b, 2H, Pyr1/HC=N), 8.28 (t, 1H, Pyr3, J = 7.6 Hz), 8.04 (d, 1H, Pyr4, J = 6.8 Hz), 7.83 (t, 1H, Pyr2, J = 4.8 Hz), 3.49 (s, 3H, CH₃); ¹³C NMR (CD₃OD): δ = 163.8 (t, C=N), 150.25 (t, Pyr1), 148.3 (q, Pyr5), 142.6 (t, Pyr3), 129.9 (t, Pyr2), 129.0 (t, Pyr4), 45.1 (p, CH₃); MS (DEI): m/z (%) = 221 (44) [M-Cl]⁺, 119 (100), 105 (9), 92 (26), 78 (14), 65 (3), 51 (10), 42 (19), 28 (5); MS (FAB): m/z $(\%) = 477 [2M-Cl]^{+} (1), 339 [2M-ZnCl_3]^{+} (22), 221 [M-Cl]^{+}$ (100); Elemental Anal. Calc. for (C₇H₈Cl₂N₂Zn, 256.450): C, 32.78; H, 3.14; N, 10.92. Found: C, 33.17; H, 3.29; N, 10.72%.

4.8. [(N-Phenyl-pyridylmethylideneamino)ZnCl₂] 2b

Anhydrous zinc(II) chloride (0.30 g, 2.2 mmol) was dissolved in 2 ml of anhydrous methanol and then a solution of **1b** (0.40 g, 2.2 mmol) in 3 ml of anhydrous methanol was added. The mixture was heated under reflux for 5 min while a yellowish solid precipitated. After stirring for an additional hour the precipitate was collected, washed with anhydrous methanol and dried in vacuo, yielding 0.58 g of yellowish 2b. Crystals, suitable for single crystal X-ray diffraction studies, were obtained by cooling a saturated solution in methanol (r.t.) to 5 °C. Yield: 83%; m.p. 300 °C (dec.); IR (Nujol): v [cm⁻¹] = 3115 w, 3092 w, 3003 w, 1594 (C=N), 1563 w, 1493 m, 1303 w, 1280 w, 1236 w, 1154 w, 1111 m, 959 w, 971 w, 916 m, 779 st, 741 m, 683 m, 650 m, 567 w, 535 m; ¹H NMR (D₆-DMSO): δ = 8.89 (d, 1H, Pyr1, *J* = 4.0 Hz), 8.68 (s, 1H, HC=N), 8.12 (t, 1H, Pyr3, *J* = 7.6 Hz), 8.07 (d, 1H, Pyr4, *J* = 7.6 Hz), 7.72 (t. 1H. Pvr2, *I* = 6.4 Hz), 7.39–7.36 (m. 2H. *m*-PhH), 7.29–7.26 (m, 3H, o,p-PhH); ¹³C NMR (D₆-DMSO): δ = 159.9 (t, C=N), 150.3 (q, Pyr5), 149.7 (t, Pyr1), 148.4 (q, PhC), 139.2 (t, Pyr3), 129.1 (t, m-PhC), 127.3 (t, Pyr2/p-PhC), 124.9 (t, Pyr4),121.4 (t, o-PhC); MS (Micro-ESI in methanol): m/z (%) = 315 (100) $[M-Cl+CH3OH]^+$, 281 (69) [M-Cl]⁺, 263 (13) [M-2Cl+OH]⁺, 247 (18) [M-2Cl+H]⁺, 181 (24); Elemental Anal. Calc. for (C₁₂H₁₀Cl₂N₂Zn, 318.520): C, 45.25; H, 3.16; N, 8.80. Found: C, 45.25; H, 3.13; N, 8.75%.

4.9. [(N-Benzyl-pyridylmethylideneamino)₃Zn(II)][ZnCl₄]·2CH₃OH 2c

Anhydrous zinc(II) chloride (0.20 g, 1.5 mmol) was dissolved in 1 ml of anhydrous methanol and a solution of 1c (0.43 g, 2.2 mmol) in 2 ml of methanol was added. The mixture was heated under reflux for five minutes and then stirred for one hour at r.t. while a colorless precipitate formed. The solid was collected, washed with anhydrous methanol and dried in vacuo, yielding 0.54 g of 2c. Crystals suitable for single crystal X-ray diffraction studies were obtained by cooling a solution saturated at r.t. in methanol to 5 °C. The product crystallized with two equivalents of methanol. Yield: 80%; m.p. 140 °C (dec.); IR (Nujol): $v \text{ [cm}^{-1}\text{]}$ = 3508 m, 3454 m, 3064 m, 3026 m, 1645 st (C=N), 1594 st, 1568 w, 1496 m, 1480 m, 1305 st, 1267 w, 1228 m, 1204 w, 1183 w, 1157 m, 1104 m, 1050 m, 1015 m, 987 w, 954 w, 920 w, 881 w, 812 w, 785 m, 770 m, 751 st, 705 st, 675 w, 638 m, 606 w, 512 w, 500 m; ¹H NMR (D₆-DMSO): δ = 8.69 (d, 1H, Pyr1, *J* = 4.0 Hz), 8.56 (s, 1H, HC=N), 8.07 (t, 1H, Pyr3, *J* = 7.2 Hz), 7.91 (d, 1H, Pyr4, *J* = 7.6 Hz), 7.65 (t, 1H, Pyr2, J = 5.6 Hz), 7.23 (s, 3H, m,p-PhH), 7.06 (s, 2H, o-PhH), 4,52 (s, 2H, CH2), 4.10 (q, 1H, methanol, J = 5.2 Hz), 3.16 (d, 3H, methanol, J = 5.2 Hz); ¹³C NMR (D₆-DMSO): $\delta = 162.1$ (t, HC=N), 149.8 (q, Pyr5), 149.2 (t, Pyr1), 139.2 (t, Pyr3), 137.0 (q, PhC), 128.3 (t, *m*-PhC), 128.1 (t, *o*-PhC), 127.2 (t, *p*-PhC), 127.0 (t, Pyr2), 124.7 (t, Pyr4), 61.6 (s, CH2), 48.6 (p, methanol); MS (positive Micro-ESI in methanol): m/z (%) = 713 (25), 491 (100) [ZnL₂Cl]⁺, 327 (21), 294 (10) [ZnLCl]⁺, 228.5 (96) [ZnL2]²⁺; MS (negative Micro-ESI in methanol): m/z (%) = 171 (100) [ZnLCl]³; Elemental *Anal.* Calc. for (C₄₁H₄₄Cl₄N₆O₂Zn₂, 925,420): C, 53.21; H, 4.79; N, 9.08. Found: C, 52.46; H, 4.88; N, 9.02%.

4.10. [(N-Allyl-pyridylmethylideneamino)ZnCl₂] 2d

Anhydrous zinc(II) chloride (0.26 g, 1.9 mmol) was dissolved in 2 ml of anhydrous methanol and a solution of **1d** (0.28 g, 1.9 mmol) in 3 ml of anhydrous methanol was added. The mixture was heated under reflux for five minutes and then stirred for one hour at r.t. Subsequently the solvent was removed in vacuo and the resulting colorless foam was stirred in 10 ml of anhydrous diethyl ether. The obtained solid was collected, washed with diethyl ether and dried in vacuo, yielding 0.47 g of 2d. Crystals suitable for single crystal X-ray diffraction studies were obtained by cooling a saturated solution in methanol (r.t.) to 5 °C. Yield: 90%; m.p. 180 °C (dec.); IR (Nujol): $v [cm^{-1}] = 3079 m$; 1650 m, 1645 m, 1598 st, 1569 m, 1477 m, 1343 w, 1302 st, 1276 w, 1224 m, 1156 m, 1117 m, 1101 m, 1045 m, 1024 m, 995 m, 973 w, 929 st, 866 w, 791 st, 648 m, 561 m, 505 m; ¹H NMR (D₆-DMSO): δ = 8.76 (b, 1H, Pyr1), 8.62 (s, 1H, HC=N), 8.23 (t, 1H, Pyr3, J = 7.6 Hz), 8.05 (d, 1H, Pyr4, J = 7.6 Hz), 7.82-7.76 (m, 1H, Pyr2), 5.80 (m, b, 1H, HC=C), 5.06-5.01 (m, 2H, C=CH₂), 4.18 (d, 2H, CH₂, J = 5.6 Hz); ¹³C NMR (D₆-DMSO): δ 161.7 (t, C=N), 149.2 (t, Pyr1), 148.3 (q, Pyr5), 140.3 (t, Pyr3), 133.9 (t, HC=C), 127.9 (t, Pyr2), 126.2 (t, Pyr4), 117.9 (s, C=CH₂), 59.5 (s, CH₂); MS (DEI): m/z (%) = 247 (15) $[M-Cl]^+$ 150 (81), 137 (100), 125 (52), 101 (88), 82 (60), 68 (24), 51 (50), 39 (62); Elemental Anal. Calc. for (C₉H₁₀Cl₂N₂Zn, 282.480): C, 38.26; H, 3.57; N, 9.92. Found: C, 38.46; H, 3.63; N, 10.04%.

4.11. X-ray structure determinations of 2a-d

The intensity data for the compounds **2a–d** were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [26,27]. The structures were solved by direct methods (SHELXS) [28] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97) [29] (Table 4). For the propene group of **2d** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [29]. XP (SIEMENS Analytical X-ray Instruments Inc.) was used for structure representations.

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Appendix A. Supplementary material

CIF files giving data collection and refinement details as well as positional parameters of all atoms have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-717944 - 717947 (see Table 4). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (home page: www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.06.044.

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