Dimeric Methylzinc Bis(2-pyridylmethyl)amide – Synthesis, Molecular Structure and Reaction with Dimethylzinc

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

The zincation of bis(2-pyridylmethyl)amine with dimethylzinc yields dimeric methylzinc bis(2-pyridylmethyl)amide (**1**) with a central Zn_2N_2 cycle with Zn-N distances of 204.8(5) and 209.8(4) pm. The Zn-C bond length of 197.0(5) pm lies in the characteristic region. The addition of dimethylzinc to **1** leads to an opening of the Zn_2N_2 cycle and the formation of tetramethyltrizinc bis[bis(2-pyridylmethyl)amide] (**2**). The dimethylzinc molecule coordinates to a pyridyl and an amide group, the C-Zn-C bond angle of 135.3(3) being rather large. In solution, compound **2** loses methane at room temperature and the intramolecular metalation product tris(methylzinc) bis(2-pyridylmethyl)amide 1,3-di(2-pyridyl)-2-azapropane-1,2-diide (**3**) precipitates. The newly formed Zn-C bond is extremely long at 219.7(5) pm.

Key words: Metalation, Pyridyl Substituents, Vicinal Dianion, Zinc
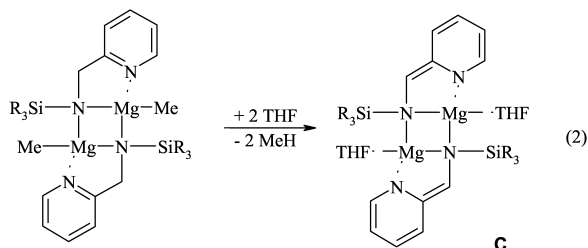
Introduction

The reaction of (2-pyridylmethyl)(trialkylsilyl)-amine with one mole equivalent of dimethylzinc yielded dimeric methylzinc-(2-pyridylmethyl) (trialkylsilyl)amide (**A**) with a central Zn_2N_2 ring [1, 2]. The addition of an excess of $ZnMe_2$ to **A** at elevated temperatures led to the evolution of methane, the precipitation of zinc and a C-C coupling reaction according to eq. (1). In order to obtain nearly quantitative yields of the C-C coupling product **B** the trialkylsilyl substituents at the nitrogen atoms were necessary. Furthermore, the thermolysis of **A** also gave the C-C coupling product in good yield. The reaction of unsubstituted 2-pyridylmethylamine with excess of dimethylzinc gave a mixture of compounds which could only be explained by transamination and subsequent C-C coupling reactions [3]. In the course of these investigations we isolated a zincated 1,4-diaza-2,3,5,6-tetrapyridylcyclohexane and therefore, we repeated these reactions with bis(2-pyridylmethyl)amine (dipicolylamine). Furthermore, 1,2-dipyridyl-1-aminoethene was isolated. No amino-imino tautomerism was observed for this molecule due to a stabilization of the amino isomer *via* in-

(1)
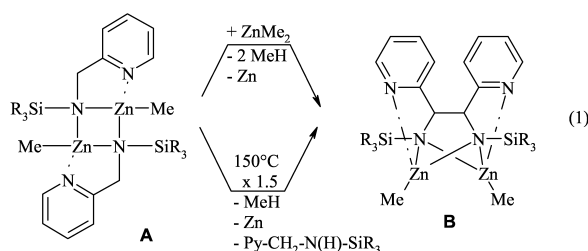
tramolecular hydrogen bonding to the pyridyl nitrogen bases [3].

The key-step of the C-C coupling reaction appears to be the metalation of the methylene group by dimethylzinc. However, this zincation occurred only at elevated temperatures. The precipitation of zinc metal was observed without the possibility to isolate any intermediates. The use of dialkylmagnesium instead of dimethylzinc allowed the isolation of an intermediate according to eq. (2), which is best described as a magnesium bis(amide) (**C** [2]).

Thus far we were unable to isolate and characterize a molecule with a deprotonated methylene group and a newly formed metal-carbon bond. Therefore, the trialkylsilyl substituent was replaced by another pyridylmethyl moiety in order to incorporate an additional co-

ordination site into the molecule. This strategy should allow the observation of intermediates because free co-ordination und hence reaction sites at the zinc atom can be blocked by the additional pyridyl base.

Results and Discussion

Synthesis

The zincation of bis(2-pyridylmethyl)amine (dipi-colylamine) gave quantitative yields of dimeric methylzinc bis(2-pyridylmethyl)amide (**1**) according to eq. (3). The zinc atoms are in distorted tetrahedral environments, the amide nitrogen being the bridging Lewis base. In the solid state one of the pyridylmethyl substituents of each ligand is not bonded to the zinc atom, however, in solution a fast exchange is observed which gives rise to only one set of NMR signals for the methylene groups (^{1}H, ^{13}C). The addition of further dimethylzinc led to the addition product tetramethyl-trizinc bis[bis(2-pyridylmethyl)amide] (**2**) which orig-inates from a rearrangement of the dimer **1**. The dimethylzinc molecule is trapped between an amide and a pyridyl nitrogen atom which enforces an open-ing of the four-membered Zn_2N_2 cycle of **1**. As a con-sequence all pyridyl groups are coordinating to zinc atoms leading to tetra-coordinated amide nitrogen and zinc atoms.

The reaction mixture was stirred at room temper-ature for approximately one hour and the evolution of methane was observed according to eq. (3). When the gas evolution stopped the reaction mixture was cooled to -18 °C and colorless crystals of **2** precip-itated and were removed from the reaction mixture. This mother liquor was stored at room temperature and tris(methylzinc) bis(2-pyridylmethyl)amide 1,3-di-2-pyridyl-2-azapropane-1,2-diide (**3**) crystallized from this blue-violet solution within several days. This com-pound can be regarded as the missing link on the way from the 2-pyridylmethylamide to the C-C-coupling product. Upon deprotonation of the methylene group a
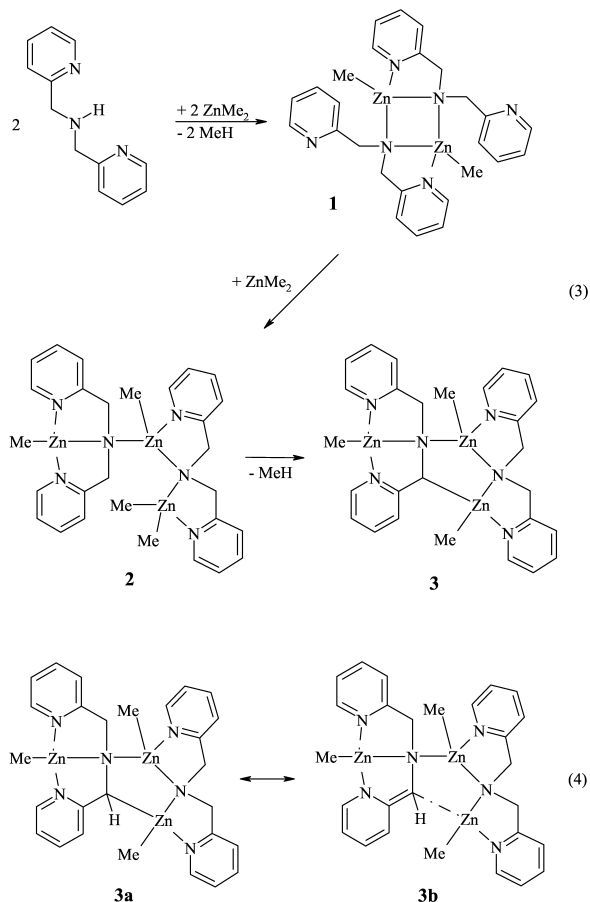
zinc-carbon bond is formed. The synthesis of **3** at room temperature prevents side reactions such as the ox-idative C-C-coupling with precipitation of zinc metal which is usually the dominant reaction path at ele-vated temperatures. The more Lewis acidic magnesium cation favors the bis(amide) resonance form according to eq. (4) [2].

Molecular structures

Methylzinc bis(2-pyridylmethyl)amide (**1**) crystal-lizes as two centrosymmetric molecules. The asym-metric unit contains two monomeric units, however, in Fig. 1 only the molecular structure and numbering scheme of one of the two molecules is depicted. Atoms generated by inversion symmetry ($-x$, $-y$, $-z + 2$) are marked with apostrophes. The endocyclic Zn-N bond lengths of 204.8 and 209.8 pm are shorter than the exocyclic coordinative bonds to the pyridyl groups (Zn1-N1 214.0 pm). The Zn1-C7 distance of 197.0 pm
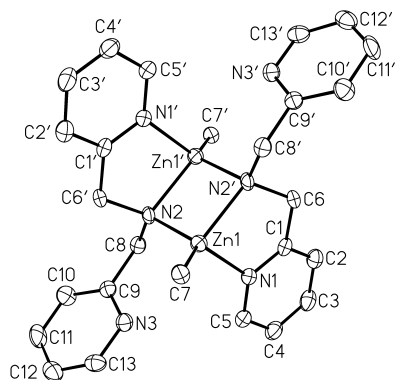
Fig. 1. Molecular structure and numbering scheme of **1**. The ellipsoids represent a probability of 30%. All hydrogen atoms are omitted for clarity reasons. Selected bond lengths [pm]: Zn1-N1 214.0(3), Zn1-N2 204.8(5), Zn1-N2' 209.8(4), Zn1-C7 197.0(5), Zn1[22c5][22c5][22c5]Zn1' 291.1(1), N2-C8 147.1(7), N2-C6' 148.1(6), C1-C6 152.5(6), C1-C2 138.2(7), C2-C3 138.2(7), C3-C4 136.6(8), C4-C5 138.7(7), N1-C5 135.6(6); angles [°]: C7-Zn1-N2 124.5(2), C7-Zn1-N2' 125.0(2), C7-Zn1-N1 124.3(2), N2-Zn1-N2' 90.8(2), N2-Zn1-N1 99.6(2), N2'-Zn1-N1 80.9(1).

also shows that there is no steric crowding at the metal atoms. Monomeric dialkylzinc without steric strain shows Zn-C distances of 193 to 195 pm [4] whereas bulky substituents such as in Zn[C{SiMe$_3$}$_3$]$_2$ (Zn-C 198.2(2) pm [5]) as well as additional Lewis bases [6] lead to an elongation of the Zn-C bonds (for example: [bpy]Zn[CH{SiMe$_3$}$_2$]$_2$, Zn-C 203.5(5) pm [6a]).

A comparison between the coordinated and the free pyridylmethyl substituents shows no significant differences of the bond lengths. The coordination of the pyridyl moiety to a zinc dication does not affect its structural parameters. However, due to ring strain the endocyclic N2'-C6-C1 angle (111.7°) is slightly smaller than the N2-C8-C9 angle (113.5°).

Fig. 2 shows the molecular structure of **2** which is the dimethylzinc adduct of **1**, however, after a rearrangement of the bis(2-pyridylmethyl)amide ligands. All three zinc atoms are bound to anionic amide nitrogen atoms, thus forming a Zn-N-Zn-N-Zn chain. We can cleave the molecule into two main fragments: on the one hand there is a monomeric methylzinc bis(2-pyridylmethyl)amide with the metal atom in a distorted tetrahedral environment, and on the other hand there is a bis(2-pyridylmethyl)amide which operates twice as a bidentate chelate base, namely to the atom Zn2 with one and to the atom Zn3 with two methyl groups. The Zn2-N2 bond between these moieties leads to a coor-
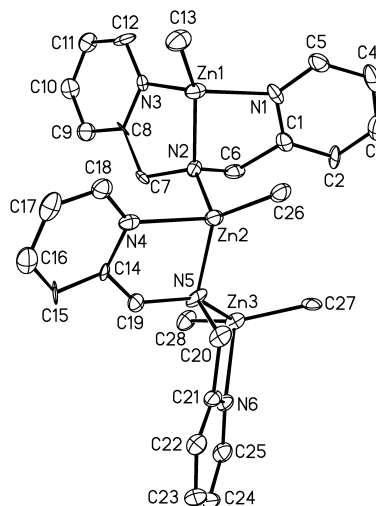

Fig. 2. Molecular structure and numbering scheme for **2**. The ellipsoids represent a probability of 30%, The H atoms are neglected for clarity reasons. Selected bond lengths [pm]: Zn1-N1 209.7(6), Zn1-N2 202.3(5), Zn1-N3 216.4(5), Zn1-C13 198.3(6), Zn2-N2 207.3(5), Zn2-N4 219.6(6), Zn2-N5 202.4(6), Zn2-C26 197.2(6), Zn3-N5 211.0(6), Zn3-N6 227.6(5), Zn2-C27 199.8(6), Zn3-C28 200.9(6); angles [°]: C13-Zn1-N2 143.2(3), C13-Zn1-N1 117.3(3), N2-Zn1-N1 83.2(3), C13-Zn1-N3 115.5(2), N2-Zn1-N3 80.8(2), N1-Zn1-N3 109.9(2), C26-Zn2-N5 123.8(2), C26-Zn2-N2 115.3(2), N5-Zn2-N2 111.4(2), C26-Zn2-N4 118.6(2), N5-Zn2-N4 81.7(3), N2-Zn2-N4 98.9(2), C27-Zn3-C28 135.3(3), C27-Zn3-N5 105.2(3), C28-Zn3-N5 112.2(3), C27-Zn3-N6 103.7(2), C28-Zn3-N6 107.0(2), N5-Zn3-N6 78.3(2).

dinative saturation and a coordination number of four for the metal and the anionic nitrogen atoms. Due to electrostatic attraction the Zn-N bonds to the anionic amide ligands are shorter than the Zn-N distances of the pyridyl fragments.

The tetrahedral environment of Zn3 is strongly distorted. The Zn-N bonds are long compared with those of Zn1 and Zn2 due to the lack of electrostatic attraction. The wide C27-Zn3-C28 bond angle fits very well into the relation between Zn-N bond lengths and CZnC angles published several years ago [6].

The molecular structure and the numbering scheme of **3** is shown in Fig. 3. All zinc and amide nitrogen atoms are embedded in tetrahedral environments. The structural fragments are similar to those of compound **2**, however, due to the newly formed Zn3-C18 bond the ZnNZnNZn chain is folded.

The most remarkable structural feature is the extremely long Zn1-C18 bond. In compound **2** all amide
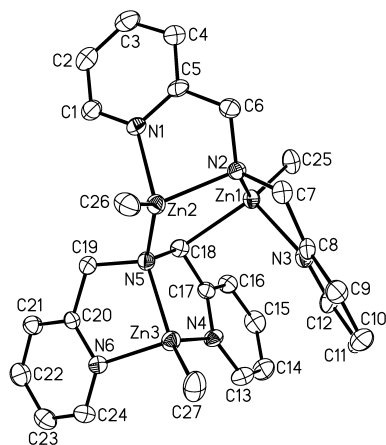
Fig. 3. Molecular structure and numbering scheme of **3**. The ellipsoids represent a probability of 30%, hydrogen atoms are not shown for clarity reasons. Selected bond lengths [pm]: Zn1-C25 198.6(6), Zn1-N2 204.6(4), Zn1-N3 213.3(4), Zn1-C18 219.7(5), Zn2-C26 198.5(6), Zn2-N5 200.0(4), Zn2-N2 204.8(4), Zn2-N1 218.8(4), Zn3-C27 195.7(6), Zn3-N4 205.5(4), Zn3-N5 205.9(4), Zn3-N6 214.6(4); angles [°]: C25-Zn1-N2 126.5(3), C25-Zn1-N3 110.4(2), N2-Zn1-N3 81.8(2), C25-Zn1-C18 124.3(2), N2-Zn1-C18 101.5(2), N3-Zn1-C18 102.0(2), C26-Zn2-N5 130.6(2), C26-Zn2-N2 113.8(2), N5-Zn2-N2 106.0(2), C26-Zn2-N1 113.5(2), N5-Zn2-N1 101.3(2), N2-Zn2-N1 79.3(1), C27-Zn3-N4 124.8(3), C27-Zn3-N5 138.6(3), N4-Zn3-N5 85.3(2), C27-Zn3-N6 118.9(3), N4-Zn3-N6 91.0(2), N5-Zn3-N6 84.0(2).

bases are four-coordinate and all pyridyl bases are already coordinating to zinc atoms. Therefore, the loss of one methyl group due to deprotonation of a methylene moiety leads to a three-coordinate zinc atom which is coordinatively unsaturated. Consequently, the Lewis-acidic zinc atom Zn1 is bonding to C18, thus forming a distorted tetrahedral coordination sphere. The Zn1-C18 bond length of 219.7(5) pm is extremely large. Longer Zn-C bonds were only reported for the lose dimer of diphenylzinc, in the crystalline state; these dimers associate to tetrameric diphenylzinc *via* interactions of the zinc atom with the phenyl π-system of a neighboring dimer [7].

Vicinal dianions are uncommon for electrostatic reasons. Here the negative charges are located on the deprotonated methylene group C18 as well as on the neighboring amide nitrogen atom N5. In Table 1 selected bond lengths and angles of the pyridylmethyl- and the pyridylmethanidyl moieties of **3** are summarized. A shortening of the C18-C17 bond compared to a C-C single bond is observed. Furthermore, a widening of the N5-C18-C17 bond angle arises. Both these

Table 1. Comparison of selected bond lengths (pm) and angles (°) of the pyridylmethylamide and pyridylmethanidyl-lamide fragments of **3**.

Pyridylmethylamide moiety		Pyridylmethanidylamide moiety	
N5-C19	147.8(6)	N5-C18	146.6(6)
C19-C20	151.4(7)	C18-C17	143.1(7)
C20-C21	139.3(7)	C17-C16	140.6(7)
C21-C22	137.3(8)	C16-C15	135.8(8)
C22-C23	136.8(8)	C15-C14	141.2(9)
C23-C24	136.4(8)	C14-C13	135.1(9)
C24-N6	134.1(7)	C13-N4	134.8(7)
N6-C20	133.7(6)	N4-C17	135.9(6)
N5-C19-C20	114.9(4)	N5-C18-C17	118.8(4)
C19-C20-C21	123.2(5)	C18-C17-C16	123.5(5)
C19-C20-N6	116.2(4)	C18-C17-N4	117.2(4)
N6-C20-C21	120.6(5)	N4-C17-C16	119.1(5)
C20-C21-C22	118.9(5)	C17-C16-C15	119.8(5)
C21-C22-C23	120.0(6)	C16-C15-C14	120.5(6)
C22-C23-C24	118.5(6)	C15-C14-C13	117.1(7)
C23-C24-N6	122.5(6)	C14-C13-N4	123.5(6)
C24-N6-C20	119.4(4)	C13-N4-C17	120.0(5)

observations support the sp^2 hybridization of the carbon atom C18 leading to a sum of its angles of 347° neglecting the C18-Zn1 bond (N5-C18-H18: 119°, C17-C18-H18: 109°). This bonding situation has an influence on the aromatic pyridyl π-system according to **3b** (eq. (4)). Consequently, also C-C bond lengths within the pyridyl fragment vary more strongly than in the pyridylmethyl moiety suggesting that the anionic charge is not solely localized on C18 but delocalized within this substituent. This fact explains the elongated Zn1-C18 bond as a consequence of a reduced electrostatic attraction between the cationic metal atom and the carbanion.

Summary and Perspective

With respect to the reaction mechanism of the zinc-mediated C-C coupling reaction compound **3** resembles the missing link going from the methylzinc pyridylmethylamide **A** to the C-C coupling product **B**, bis(methylzinc) 1,2-dipyridyl-1,2-diamide. Whereas the C-C coupling reaction is accompanied by the precipitation of zinc metal, this reduction of the metal is prevented in this case by the coordinative saturation of the zinc atoms by other Lewis-nitrogen bases.

Experimental Section

General procedures

All experiments and manipulations were carried out under an atmosphere of argon. Reactions were performed by using

standard Schlenk techniques and in dried, thoroughly deoxygenated solvents. For the numbering scheme of the pyridyl substituent refer to Fig. 4.
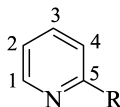
Fig. 4. Numbering scheme of the pyridyl fragment for the assignment of the NMR data.

Dimeric methylzinc bis(2-pyridylmethyl)amide (1)

Bis(2-pyridylmethyl)amine (3.60 ml, 20.0 mmol) was dissolved in 20.0 ml of toluene. At 0 °C 10.0 ml of a 2.0 molar dimethylzinc solution (20.0 mmol) in toluene was added dropwise and the evolution of a gas was observed immediately. The violet solution was stirred over night and slowly warmed up to room temperature. After reduction of the volume at r. t. and under reduced pressure 4.62 g of colorless crystals of **1** (8.3 mmol, 82%) precipitated during the storage of the mother liquor at approximately 5 °C. M.p.: 126 °C (dec.). – ^{1}H NMR ([D$_6$]benzene): $\delta = 8.47$ (Pyr 1, ddd, 2 H, $^3J_{H,H} = 5.0$ Hz, $^4J_{H,H} = 1.7$ Hz, $^5J_{H,H} = 0.9$ Hz); 6.92 (Pyr 3, ddd, 2 H, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 2.0$ Hz); 6.84 (Pyr 4, d, 2 H, $^3J_{H,H} = 7.60$ Hz); 6.47 (Pyr 2, m, 2 H); 4.24 (CH$_2$, s, 2 H); −0.28 (ZnCH$_3$, s, 3 H). – ^{13}C{^{1}H} NMR ([D$_6$]benzene): $\delta = 164.0$ (Pyr 5); 148.2 (Pyr 1); 136.1 (Pyr 3); 121.9 (Pyr 2); 121.1 (Pyr 4); 60.8 (CH$_2$); −17.1 (ZnCH$_3$). – IR: 1645 w, 1601 vs, 1591 vs, 1569 vs, 1524 vw, 1512 w, 1478 vs, 1433 vs, 1411 s, 1377 w, 1356 m, 1340 vs, 1292 vs, 1284 vs, 1262 s, 1229 vs, 1208 s, 1152 vs, 1142 vs, 1125 vs, 1099 vs, 1092 vs, 1030 s, 1015 vs, 996 vs, 979 s, 963 m, 956 m, 947 m, 920 vs, 894 m, 882 m, 836 s, 813 s, 757 vs, 731 vs, 701 w, 636 vs, 626 vs, 518 s, 508 vs, 498 vs, 476 vs, 464 s, 434 m, 405 vs, 384 s, 371 m, 289 w, 281 m, 267 w. – Elemental analysis for [C$_{13}$H$_{15}$N$_3$Zn]$_2$ (557.32): calcd. C 56.03, H 5.43, N 15.08; found C 54.52, H 5.26, N 14.56. – MS (EI, *m/z*, relative intensities in brackets [%]): 278 (M$^+$ of the monomer, 2), 200 (51), 184 (9), 121 (6), 107 (38), 93 (100), 78 (9), 65 (8), 39 (6).

Tetramethyltrizinc bis[bis(2-pyridylmethyl)amide] (2)

A solution of dimethylzinc (3.75 ml, 2.0 molar, 7.5 mmol) in toluene was added dropwise at 0 °C to a magnetically stirred solution of 0.9 ml of di(2-pyridylmethyl)amine (5.0 mmol) in 10 ml of toluene. After addition of the zincation reagent the reaction mixture turned from yellow to blue-violet under evolution of methane. This solution was stirred for 1 h at r. t. and then stored at −18 °C. Colorless crystals of **2** (0.5 g, 0.8 mmol, 32%) were isolated. M.p.: 254 °C (dec.).

Table 2. Crystallographic data of **1**, **2** und **3** as well as details of the structure solution and refinement procedures.

Compound	1	2	3
Formula	C$_{26}$H$_{30}$N$_6$Zn$_2$	C$_{28}$H$_{36}$N$_6$Zn$_3$	C$_{27}$H$_{32}$N$_6$Zn$_3$
Formula mass [g mol^{-1}]	557.30	652.74	636.70
T [K]	193(2)	193(2)	193(2)
Crystal system	triclinic	triclinic	monoclinic
Space group [8]	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a [pm]	964.50(9)	1040.5(2)	1102.61(8)
b [pm]	1065.24(9)	1107.8(2)	1949.0(2)
c [pm]	1295.4(1)	1385.7(2)	1268.1(1)
α [°]	91.590(2)	86.141(3)	90
β [°]	102.446(2)	77.558(4)	109.293(2)
γ [°]	98.037(2)	71.160(2)	90
V [nm^3]	1.2845(2)	1.4760(4)	2.7749(4)
Z	2	2	4
d_{ber} [g cm^{-3}]	1.441	1.469	1.524
μ [mm^{-1}]	1.893	2.445	2.599
$F(000)$	576	672	1304
Scan range [°]	3.8<2θ<46.5	3.0<2θ<46.6	3.8<2θ<46.6
Collected data	1911	6638	12322
Unique data N$_o$	1828	3425	3598
Absorption correction	none	SADABS	SADABS
T$_{min}$/T$_{max}$	–	0.817/1.000	0.795/1.000
Restraints	0	0	0
Parameters N$_p$	309	370	453
N$_o$/N$_p$	5.9	9.3	7.9
wR_2 (on F^2, all data)^a	0.0801	0.0640	0.0870
R-values^a ($I > 2\sigma(I)$) data	1529	1649	2934
wR_2 on F^2	0.0747	0.0598	0.0801
R_1	0.0299	0.0361	0.0359
GOF^b s on F^2	1.008	0.686	1.067
Res. electron dens. density [e nm^{-3}]	294/ − 224	324/ − 298	442/ − 446
CCDC-number [12]	225323	225324	225325

^{a} $R_1 = (\Sigma\|F_o| - |F_c\|) / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$ mit $w^{-1} = \sigma^2(F_o^2) + (aP)^2$; ^{b} $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

– ^{1}H NMR ([D$_6$]benzene): $\delta = 8.14$ (Pyr 1, s, br, 4 H); 7.45 to 7.28 (Pyr 3, m, br, 4 H); 6.88 to 6.66 (Pyr 4, m, br, 4 H); 6.46 (Pyr 2, m, br, 4 H); 4.13 (CH$_2$, s, br, 8 H); −0.15 (ZnCH$_3$, s, br, 12 H). – ^{13}C{^{1}H}-NMR ([D$_6$]benzene): $\delta = 163.8$ (Pyr 5); 147.1 (Pyr 1); 137.6 (Pyr 3); 122.6 (Pyr 2); 121.9 (Pyr 4); 59.9(CH$_2$); −18.1 (ZnCH$_3$, br). – IR: 1591 vs, 1569 s, 1474 s, 1434 vs, 1411 m, 1356 w, 1291 w, 1261 vw, 1199 vw, 1148 w, 1117 w, 1094 w, 1048 m, 1017 w, 994 m, 889 w, 849 w, 759 vs, 700 w, 628 w, 482 s, 404 s. – Elemental analysis for C$_{28}$H$_{36}$N$_6$Zn$_3$ (652.77): calcd. C 51.52, H 5.56, N 12.88; found C 47.14, H 4.76, N 12.70 (The C and H values obtained are low due to the loss of methane during the heating).

*Tris(methylzinc) bis(2-pyridylmethyl)amide 1,3-di-2-pyridyl-2-azapropane-1,2-diide (**3**)*

A solution of dimethylzinc (3.75 ml, 2.0 molar) in toluene was added dropwise to a magnetically stirred solution of 0.9 ml of di(2-pyridylmethyl)amine (5.0 mmol) in 10 ml of toluene at 0 °C. After the addition of the dimethylzinc solution the reaction mixture turned from yellow to blue-violet under development of methane gas. The mixture was stirred for an additional hour at r. t. Then the solution was stored at -18 °C and 0.5 g of colorless crystals of **2** were obtained. The mother liquor was decanted and after 2 d. at r. t. 0.8 g of red-violet crystals of **3** (1.3 mmol, 52%) precipitated at r. t. Mp.: $55-56$ °C. – ^{1}H NMR ([D$_6$]benzene): $\delta = 8.47$, 8.34, 7.95, 7.49 to 7.32, 6.91 to 6.55, 6.35, 5.84 (multiplets of the pyridyl groups, assignment due to overlapping and coverage by the solvent signals not possible), 4.88, 4.58, 4.00, 3.79 (CH$_2$, d, $^2J_{H,H} = 16$ Hz, 4 H), 4.25 (CH$_2$, d, $^2J_{H,H} = 5.6$ Hz, 2 H), 3.98 (CH, s, 1 H), -0.45, -0.63, -0.73 (ZnCH$_3$, s, 9 H). – ^{13}C$\{^1$H$\}$ NMR ([D$_6$]benzene): $\delta = 171.1$, 164.7, 162.6, 161.7 (Pyr 5); 147.7, 147.1, 146.3 (Pyr 1); 137.5, 137.3, 136.8 133.3 (Pyr 3); 122.2, 122.1, 121.9, 121.8, 121.7, 121.6 (Pyr 2, Pyr 4), 116.2, 108.2, 84.2 (Pyr, CH); 66.9, 61.6, 60.5 (CH$_2$), -18.0 (br), -18.4 (ZnCH$_3$). – Elemental analysis for C$_{27}$H$_{32}$N$_6$Zn$_3$ (636.73): calcd. C 50.93, H 5.07, N 13.20; found C 49.30, H 4.99, N 12.70.

X-ray structure determinations

Data was collected on a Siemens P4 diffractometer with a CCD area detector using graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 71.073$ pm). Oil-coated single crystals were rapidly cooled, mounted and centered on the diffractometer. Crystallographic parameters, details of data collection and refinement procedures are summarized in Table 2.

All structures were solved by direct methods and refined with the software package SHELXL-97 [9]. Neutral scattering factors were taken from Cromer and Mann [10] and for the hydrogen atoms from Stewart et al. [11] The non-hydrogen atoms were refined anisotropically. The H-atoms were considered with a riding model under restriction of ideal symmetry at the corresponding atoms.

Supporting information available

X-ray crystallographic files in CIF format. This material is available free of charge from the Cambridge Crystallographic Data Centre [12].

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[12] Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-225323 for **1**, -225324 for **2**, and -225325 for **3**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].