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Synthesis and Crystal Structures of Dinuclear Zinc Complexes with the 3,5-Bis(pyridine-2-yl)pyrazolato Ligand

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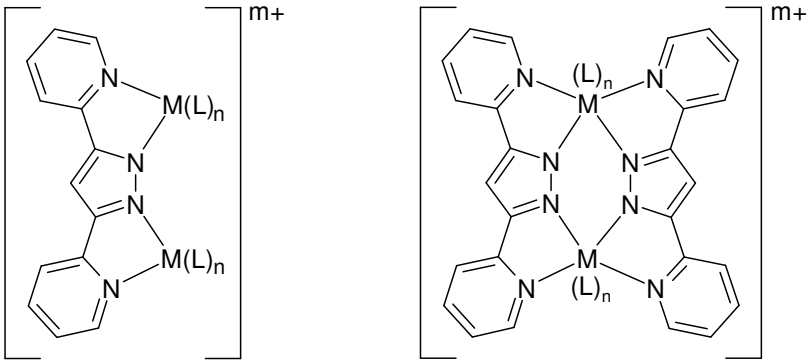
Abstract

Zincation of 3,5-bis(pyridine-2-yl)pyrazole with $Zn[E(SiMe_3)_2]_2$ in tetrahydrofuran yields dimeric 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)amide (E = N, **1**) and bis(trimethylsilyl)methanide (E = CH, **2**). These complexes crystallize in the space groups $P2_1/n$ and $P\bar{1}$, respectively. The zinc atoms are in distorted tetrahedral environments. In the solid state the 3,5-bis(pyridine-2-yl)pyrazolato anions act as bridging tridentate bases with one pyridyl group not participating in the coordination behaviour. In solution exchange processes fast on the NMR time scale lead to a single set of resonances for the pyridyl substituents.

Introduction

Dinuclear zinc complexes play an important role in biomimetic models for enzymes and catalysts [1]. Often pyridyl groups are used to mimic N-bound histidine bases. In the course of our investigations of dinuclear zinc complexes with multi-dentate ligands such as 1,2-bis(pyridine-2-yl)-1,2-diamidoethanes [2] or bis(2-pyridylmethyl)amides [3] we included studies with tetradentate 3,5-bis(2-pyridyl)pyrazolato anions. Pyrazolyl and imidazolyl units also play a crucial role in bioinorganic chemistry of zinc in order to mimic active sites of zinc enzymes [4]. 3,5-Substituted pyrazolate ligands represent valuable bridging units between two zinc ions with a strong influence of the side arms (length and nature of functional groups) on the catalytic activity [5]. An easily accessible ligand offering pyrazolyl as well as pyridyl functionalities is the well-known 3,5-bis(pyridine-2-yl)pyrazolate anion. This ligand forms complexes with the late 3d transition metals from Cr to Cu whereas no examples are known for the earlier transition metals [6]. Only hydrates of 3,5-bis(2-pyridyl)pyrazole zinc halide [7] and nitrate [7, 8] and their homologous cadmium derivatives are reported, however, the molecular structures remained unknown. The rigidity of this 3,5-bis(2-pyridyl)pyrazolyl

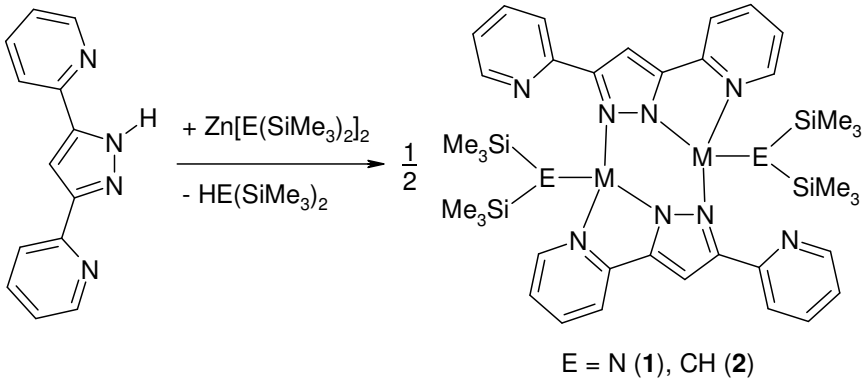
ligand enables the formation of dinuclear metal complexes and in some cases even complexes of higher nuclearity via self-assembly [9]. In general, the 3,5-bis(pyridine-2-yl)pyrazolato ligand acts as a bridging ligand and in bidentate fashion to both the metal cations as displayed in Scheme 1. In these complexes the metals often show hexa-coordination in distorted octahedral environments.



Scheme 1: Common coordination modes of the 3,5-bis(pyridine-2-yl)pyrazolate anion as a bridging ligand. The value of m depends on the oxidation state on M and on the charge of L (which can be solvent molecules and counter anions).

Results and Discussion

3,5-Bis(pyridine-2-yl)pyrazole was deprotonated with $Zn[E(SiMe_3)_2]_2$ (E = N, CH) in tetrahydrofuran yielding 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)amide (E = N, **1**) and bis(trimethylsilyl)methanide (E = CH, **2**), respectively, according to equation 1. These isotypic compounds were recrystallized from concentrated thf solutions to grow single crystals suitable for X-ray structure determinations.



(1)

NMR spectroscopic data are summarized in Table 1. The numbering scheme is in accordance with the IUPAC recommendation. The amide or methanide groups show nearly no influence

on the ^{1}H NMR data of the 3,5-bis(pyridine-2-yl)pyrazolato anions of **1** and **2**. However, the $^{13}C\{^{1}H\}$ NMR parameters of the central pyrazolato ring differ strongly. This fact can be explained by a reduced charge on the zinc atoms for the bis(trimethylsilyl)methyl derivative **2**. The zinc atoms bind tightly to the nitrogen bases and therefore the charge on the metal atoms influences the chemical shifts of the N-bound carbon atoms the most.

Insert Table 1

Molecular structures and numbering schemes of isoelectronic **1** and **2** are shown in Figures 1 and 2, respectively. The molecular structures are very similar even though they do not crystallize isomorphous. In both compounds the 3,5-bis(pyridine-2-yl)pyrazolato anions show a rather unique coordination behaviour. The bridging pyrazolato moiety is bound to two zinc cations. The metal atoms also coordinate to one pyridyl group (forming a five-membered ZnN_2C_2 heterocycle) whereas the other pyridyl substituent is not involved in the ligand sphere of the zinc atom as shown in equation 1.

Insert Figures 1 and 2
Insert Table 2

Selected structural data of **1** and **2** are compared in Table 2. In both complexes the endocyclic Zn1-N1/N2 and Zn2-N5/N6 bond lengths are significantly larger than the exocyclic Zn1-N7 and Zn2-N3 distances. Ring formation also leads to narrow N1-Zn1-N2 and N5-Zn2-N6 bond angles of 76.9°. In **1** the Zn-N bonds to the bis(trimethylsilyl)amide anions show the smallest values due to a rather large electrostatic attraction. Nevertheless, in $Zn[N(SiMe_3)_2]_2$ with a two-coordinate zinc atom significantly smaller Zn-N bond lengths are observed (Zn-N, solid state: 183.3(11) pm [10], gas phase: 182.4(14) pm [11]). The influence of the coordination numbers of Zn and N on the Zn-N distances is nicely shown for a number of homoleptic zinc amides of the type $Zn[N(SiR_3)R']_2$ [12] and $Zn(NPh_2)_2$ [13]. The bulkiness of the $E(SiMe_3)_2$ ligands (E = CH, N) induces steric pressure and enhanced N-Zn-E angles in **1** and **2**. The negative charge of the pyrazolato anions are delocalized within this five-membered aromatic ring which reduces the negative charge on the nitrogen atoms N2, N3 as well as N6, N7. Even though the 3,5-bis(pyridine-2-yl)pyrazolato ligand displays a nearly planar arrangement there is nearly no charge delocalization into the pyridyl moieties; the C-C bonds between the aromatic rings show values of approximately 146.6 pm which is characteristic for single

bonds between sp^2 hybridized carbon atoms. The Zn-C distances of 201.3 pm are rather large and represent a characteristic value for dialkylzinc with tetra-coordinate metal atoms [14].

Conclusion and Perspective

In the solid state only one of the pyridyl groups of the anion is bound to zinc. However, in solution an exchange reaction, which is fast on the NMR time scale, leads to two chemically equivalent pyridyl substituents and one set of resonances. The tendency of zinc to favour tetra-coordination leads to unique molecular structures for **1** and **2** which were unknown for the 3,5-bis(pyridine-2-yl)pyrazolato anions as of yet but they are comparable to complexes of the type $[RZn\text{-}N(CH_2Py)_2]_2$ [3]. In these compounds only one set of NMR signals was found for the pyridyl groups but in the solid state only one pyridyl substituent was acting as a Lewis base to the zinc cations.

The catalytic activity of $[RZn\text{-}N(CH_2Py)_2]_2$ is based on the fact that the pyridyl groups can act as hemilabile Lewis bases [15]. However, the hydrogen atoms at the α-methylene units are rather acidic and deprotonation reactions can occur leading to by-products [3]. This kind of side-reaction is impossible for the 3,5-bis(pyridine-2-yl)pyrazolato ligand. Therefore further investigations are in progress in order to evaluate the catalytic activity of **1** and **2** because these complexes fulfil the pre-condition that hemilabile ligands offer access to the metal centers.

Experimental

All manipulations were carried out in an anaerobic argon atmosphere and the solvents were thoroughly dried. IR spectra were recorded with Nujol solutions between KBr windows. The values of the elemental analysis deviate from theoretical values because weighing of these moisture sensitive compounds was challenging due to the easy loss of cocrystallized thf and also due carbonate formation during combustion even though V_2O_5 was added. Starting 3,5-bis(pyridine-2-yl)pyrazole [8], $Zn[N(SiMe_3)_2]_2$ [16], and $Zn[CH(SiMe_3)_2]_2$ [17] were prepared according to literature procedures.

Synthesis of 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)amide (**1**): 3,5-Bis(pyridine-2-yl)pyrazole (570 mg, 5.56 mmol) were dissolved in 15 ml of thf and cooled to –30°C. Zinc bis[bis(trimethylsilyl)amide] (2.5 g, 6.49 mmol), dissolved in 15 ml of thf and also cooled to –30°C, was added dropwise. The reaction mixture was stirred for further 5 h

and then warmed to r.t. The formed precipitate was redissolved at 50°C and the solution slowly cooled again to r.t. Crystallization of **1** was completed by storing of the reacton mixture at 4 °C for 2 d. Yield: 980 mg of **1** (2,19 mmol 85,5%). – Dec. above 238°C. – ^{1}H NMR ([D$_8$]THF) δ = 8.93 (d, ^{3}J(H^{8,14},H^{9,15}) = 4.8 Hz, 2H, Pyr^{8,14}); 7.83 (ddd, ^{3}J(H^{10,16},H$^{9,11;15,17}$) = 7.7 Hz, ^{4}J(H^{10,16},H^{8,14}) = 1.5 Hz, 2H, Pyr^{10,16}); 7.66 (d, ^{3}J(H^{11,17},H^{10,16}) = 7.9 Hz, 2H, Pyr^{11,17}); 7.35 (ddd, ^{3}J(H^{9,15},H$^{10,16;8,14}$) = 5.4 Hz, ^{4}J(H^{9,15},H^{11,17}) = 0.8 Hz, 2H, Pyr^{9,15}); 7.05 (s, 1H, H^{4}); 0.06 (s, 18H, H^{Me}). – ^{13}C NMR ([D$_8$]THF) δ = 146.7 (Pyr^{8,14}); 144.7 (Pyr^{6,12}); 136.4 (Pyr^{10,16}); 133.6 (C^{3,5}); 120.1 (Pyr^{9,15}); 117.5 (Pyr^{11,17}); 96.4 (C^{4}); 3.5 (C^{Me}). – IR (Nujol, cm^{-1}): ν = 3378 w, 3115 w, 3053 m, 2920 vs, 2720w, 2683 m, 2609 w, 2532 w, 2308 m, 1979 m, 1850 m, 1767 m, 1705 m, 1652 w, 1606 vs, 1568 s, 1536 s, 1456 s, 1436 s, 1378s, 1366 w, 1345 s, 1274 w, 1249 vs, 1180 m, 1151s, 1141 m, 1095 m, 1074 m, 1048 w, 1020 w, 1009 w, 987 s, 884 s, 766 s, 738 m, 696 m, 663 s, 639 m, 625 m, 613 m, 552 m, 504 w, 497 m, 470 m, 462w. – MS (EI): *m/z* (%) = 384* (1.4), 369* (9), 275 (48), 161 (7), 147 (29), 146 (100) [(Me$_3$Si)$_2$, HNSi$_2$Me$_5$, Si$_2$Me$_6$]$^{+}$, 130 (41), (signals with an asterisk * show the isotopic pattern of Zn). – Elemental analysis (C$_{19}$H$_{27}$N$_5$Si$_2$Zn(thf), 519.13): calcd.: C 53.11, H 6.98, N 13.46; found: C 52.28, H 6.16, N 13.62.

Synthesis of 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)methanide (**2**): A solution of zinc bis[bis(trimethylsilyl)methanide] (400 mg, 1.04 mmol) in 5 ml of toluene was dropped into a solution of 3,5-bis(pyridine-2-yl)pyrazole (228 mg, 1.03 mmol) in 5 ml of thf. Then the reaction mixture was heated to 60 °C for 30 min and thereafter slowly cooled to r.t. The product crystallized in the shape of colorless cubes. Yield: 420 mg of **2** (0,94 mmol, 91%). – Dec. above 260°C. – ^{1}H NMR ([D$_8$]THF) δ = 8.92 (d, ^{3}J(H^{8,14},H^{9,15}) = 5.0 Hz, 2H, Pyr^{8,14}); 7.78 (ddd, ^{3}J(H^{10,16},H$^{9,11;15,17}$) = 7.1 Hz, ^{4}J(H^{10,16},H^{8,14}) = 1.8 Hz, 2H, Pyr^{10,16});

7.65 (d, $^{3}J(H^{11,17},H^{10,16})$ = 8.0 Hz, 2H, $Pyr^{11,17}$); 7.29 (ddd, $^{3}J(H^{9,15},H^{10,16;8,14})$ = 6.6 Hz, $^{4}J(H^{9,15},H^{11,17})$ = 1.6 Hz, 2H, $Pyr^{9,15}$); 7.02 (s, 1H, H^{4}); 0,10 (s, 1H, H^{19}); -0.14 (s, 18H, H^{Me}). – ^{13}C-NMR ([D_8]THF) δ = 152.4 ($Pyr^{6,12}$); 151.1 ($Pyr^{8,14}$); 138.9 ($Pyr^{10,16}$); 122.7 ($Pyr^{9,15}$); 120.6 ($Pyr^{11,17}$); 109.6 ($C^{3,5}$); 100.0 (C^{4}); 4.9 (C^{Me}); 1.3 (C^{19}). – IR (Nujol, cm^{-1}): ν = 3556 vw, 3118 w, 3046 w, 2852 s, 2722 w, 2667 w, 2309 vw, 1976 w, 1912 w, 1842 w, 1766 w, 1686 w, 1649 w, 1606 vs, 1590 w, 1565 s, 1533 s, 1454 vs, 1435 vs, 1377 s, 1343 m, 1276 m, 1255 w, 1236 vs, 1150 m, 1135 m, 1095 w, 1072 m, 1049 m, 1027 s, 1019 s, 1007 s, 989 m, 974 m, 897 s, 853 s, 801 m, 765 s, 742 s, 708 w, 695 w, 671 s, 638 m, 622 m, 609 m, 550 m, 497 m, 476 w, 467 m. –MS (EI): *m/z* (%) = 444* (28) $[M]^{+}$, 429* (100) $[M\text{-}CH_3]^{+}$, 367* (8) $[M\text{-Pyridyl}]^{H+}$, 357* (11) $[429H\text{-}SiMe_3]^{H+}$, 335 (23), 286* (12), 273 (16), 145 (34), 129 (42), (signals with an asterisk * show the isotopic pattern of Zn). – Elemental analysis ($C_{20}H_{28}N_4Si_2Zn$, 446.05): calcd.: C 53.74, H 6.54, N 12.53; found: C 53.56, H 6.35, N 12.61.

Crystal structure determination: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated MoK_α radiation [18, 19]. The structures were solved by Direct Methods (SHELXS [20]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [21]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically [21]. Crystallographic data as well as structure solution and refinement details are summarized in Table 3. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

Insert Table 3

Acknowledgement

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Supporting Information available: Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-773037 for **1**, and CCDC-773037 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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Table 1: NMR data of 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)amide (E = N, **1**) and bis(trimethylsilyl)methanide (E = CH, **2**) ([D_8]thf, 25°C).

	1 (E = N)		**2** (E = CH)	
	^{1}H	**^{13}C{^{1}H}**	**^{1}H**	**^{13}C{^{1}H}**
C3/5	-	133.6	-	109.6
C4-H	7.05	96.4	7.02	100.0
C6/12	-	144.7	-	152.4
C8/14-H	8.93	146.7	8.92	151.1
C9/15-H	7.35	120.1	7.29	122.7
C10/16-H	7.83	136.4	7.78	138.9
C11/17-H	7.66	117.5	7.65	120.6
$CHSi_2$	-	-	0.10	1.3
$SiMe_3$	0.06	3.5	-0.14	4.9

Table 2: Structural parameters of the metal environments in **1** and **2** (bond lengths [pm] and angles [deg.]).

	1 (E = N)	**2** (E = CH)
Zn1-N1	211.3(2)	213.1(3)
Zn1-N2	213.3(2)	209.3(2)
Zn1-N7	201.0(2)	205.7(3)
Zn1-E	192.3(2)	201.2(3)
Zn2-N3	203.1(2)	202.4(3)
Zn2-N5	212.3(2)	214.0(2)
Zn2-N6	208.6(2)	212.1(3)
Zn2-E	192.8(2)	201.3(3)
E-Si1	170.6(2)	184.9(3)
E-Si2	171.6(2)	184.7(3)
E-Si3	170.9(2)	185.2(3)
E-Si4	170.9(2)	185.0(3)
N1-Zn1-N2	76.72(7)	77.13(10)
N1-Zn1-N7	118.83(8)	116.89(19)
N1-Zn1-E	112.74(8)	120.48(11)
N2-Zn1-N7	87.04(7)	88.77(10)
N2-Zn1-E	123.67(8)	120.32(11)
N7-Zn1-E	124.86(8)	119.61(12)
N3-Zn2-N5	120.61(7)	119.79(10)
N3-Zn2-N6	87.85(8)	88.73(10)
N3-Zn2-E	126.17(8)	119.09(12)
N5-Zn2-N6	76.92(7)	76.76(10)
N5-Zn2-E	108.52(8)	118.23(12)
N6-Zn2-E	125.47(8)	121.31(12)

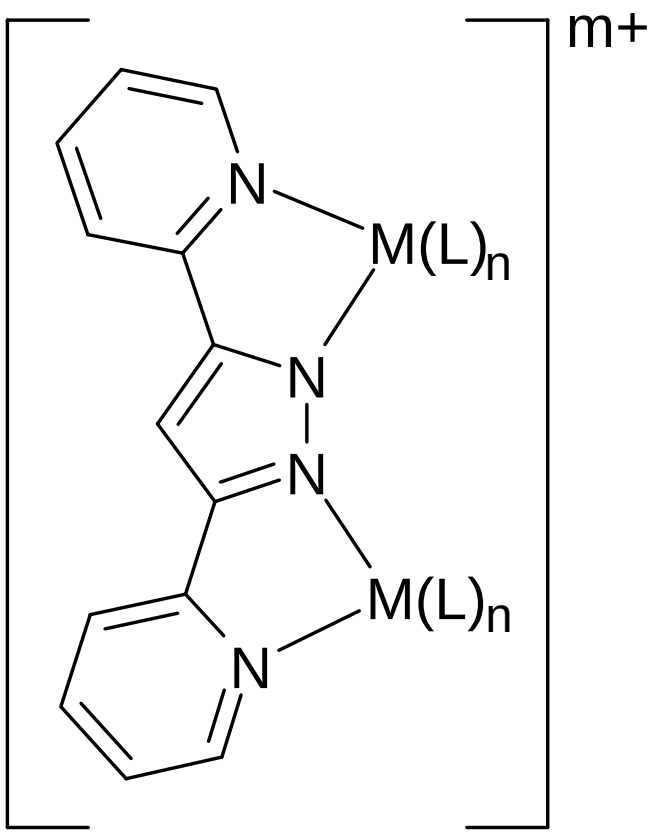
Table 3: Crystal data and refinement details for the X-ray structure determinations of **1** and **2**.

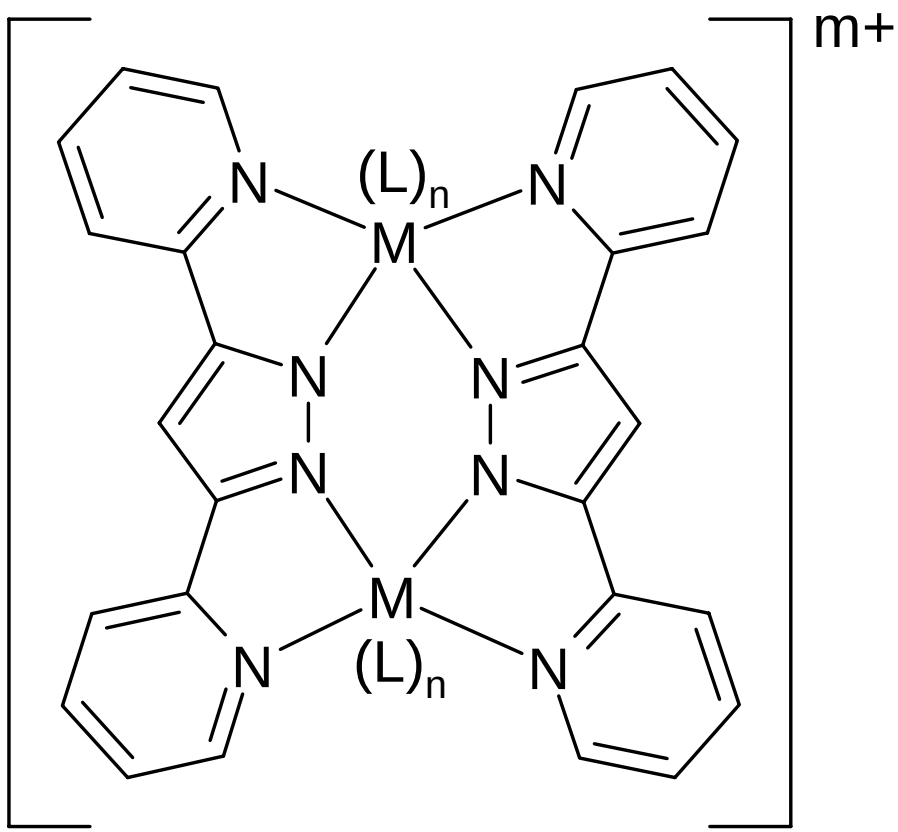
	1 (E = N)	**2** (E = CH)
Formula	$C_{38}H_{54}N_{10}Si_4Zn_2$, $2(C_4H_8O)$	$C_{40}H_{56}N_8Si_4Zn_2$, $1.5(C_4H_8O)$
Fw ($g \cdot mol^{-1}$)	1038.22	1000.18
T/K	-140(2)	-90(2)
Crystal system	monoclinic	triclinic
Space group	$P\,2_1/n$	$P\,\bar{1}$
a/ Å	13.3555(3)	13.7044(4)
b/ Å	26.3010(5)	14.1141(5)
c/ Å	15.1101(2)	15.5526(6)
α/°	90	74.086(1)
β/°	95.157(1)	70.244(2)
γ/°	90	85.002(2)
V/Å^3	5286.13(17)	2722.64(16)
Z	4	2
σ ($g \cdot cm^{-3}$)	1.305	1.220
μ (cm^{-1})	10.44	10.09
Measured data	35385	19659
Data with $I > 2\sigma(I)$	8038	8875
unique data / R_{int}	12098/0.0621	12342/0.0331
wR_2 (all data, on F^2)[a)]	0.0929	0.1512
R_1 ($I > 2\sigma(I)$)[a)]	0.0407	0.0484
s[b)]	0.995	1.013
Res. dens./e·Å^{-3}	0.686/-0.417	1.039/-0.547
CCDC No.	773037	773038

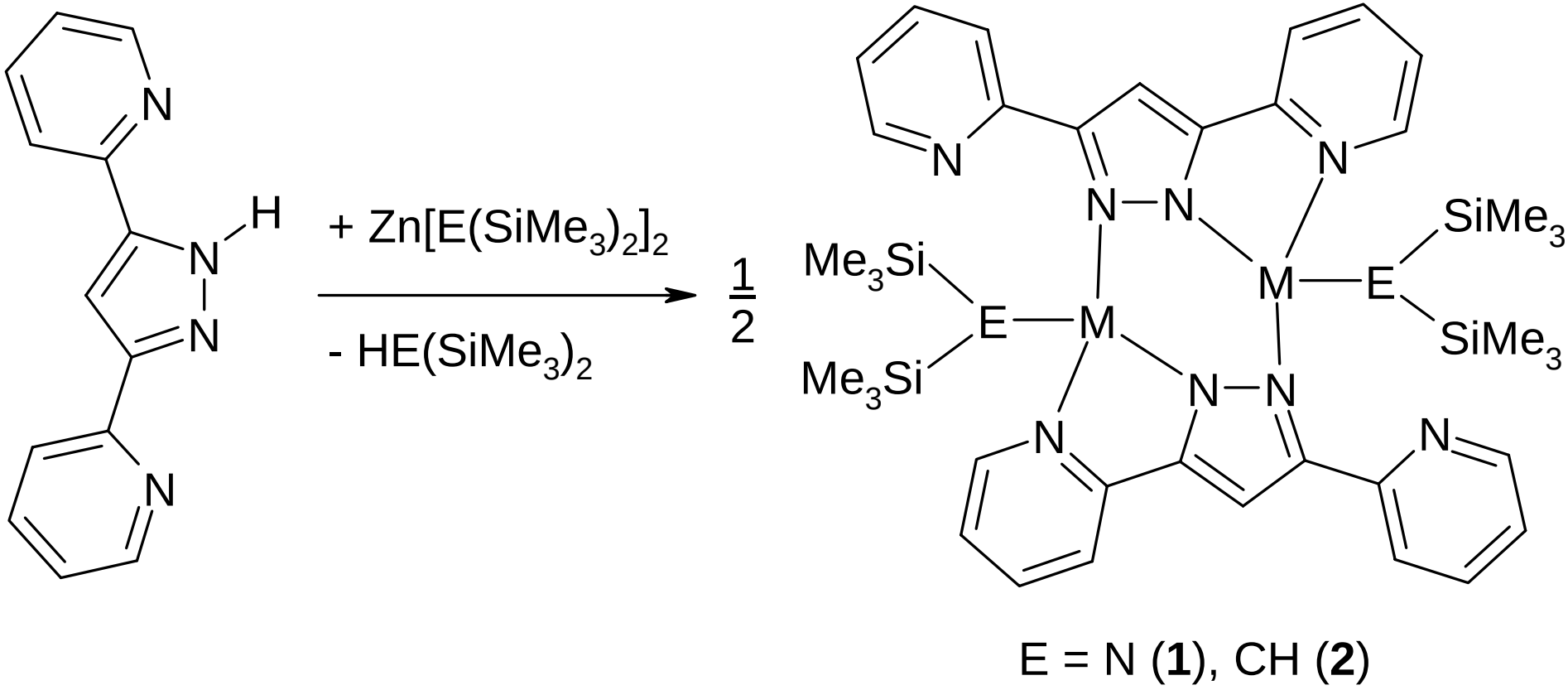
[a)] Definition of the R indices: $R_1 = (\Sigma \,||\, F_o| - |F_c|\,|)/\Sigma|F_o|$;
$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2)]/3$;
[b)] $S = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

Figure 1: Molecular structure and numbering scheme of 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)amide (**1**). The ellipsoids represent a probability of 40%, H atoms are neglected for clarity reasons.

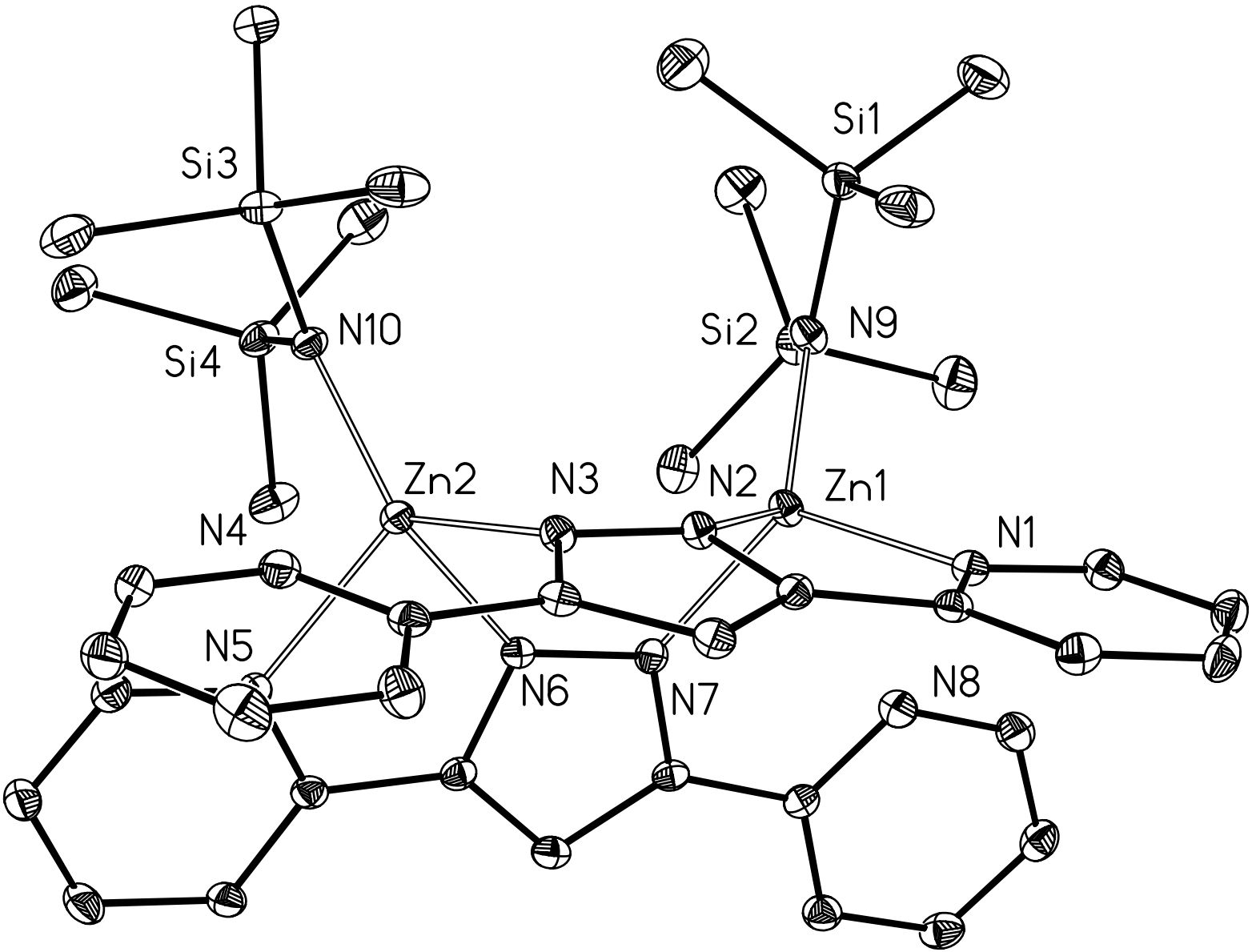
Figure 2: Molecular structure and numbering scheme of 3,5-bis(pyridine-2-yl)pyrazolato zinc bis(trimethylsilyl)methanide (**2**). The ellipsoids represent a probability of 40%, hydrogen atoms are omitted.

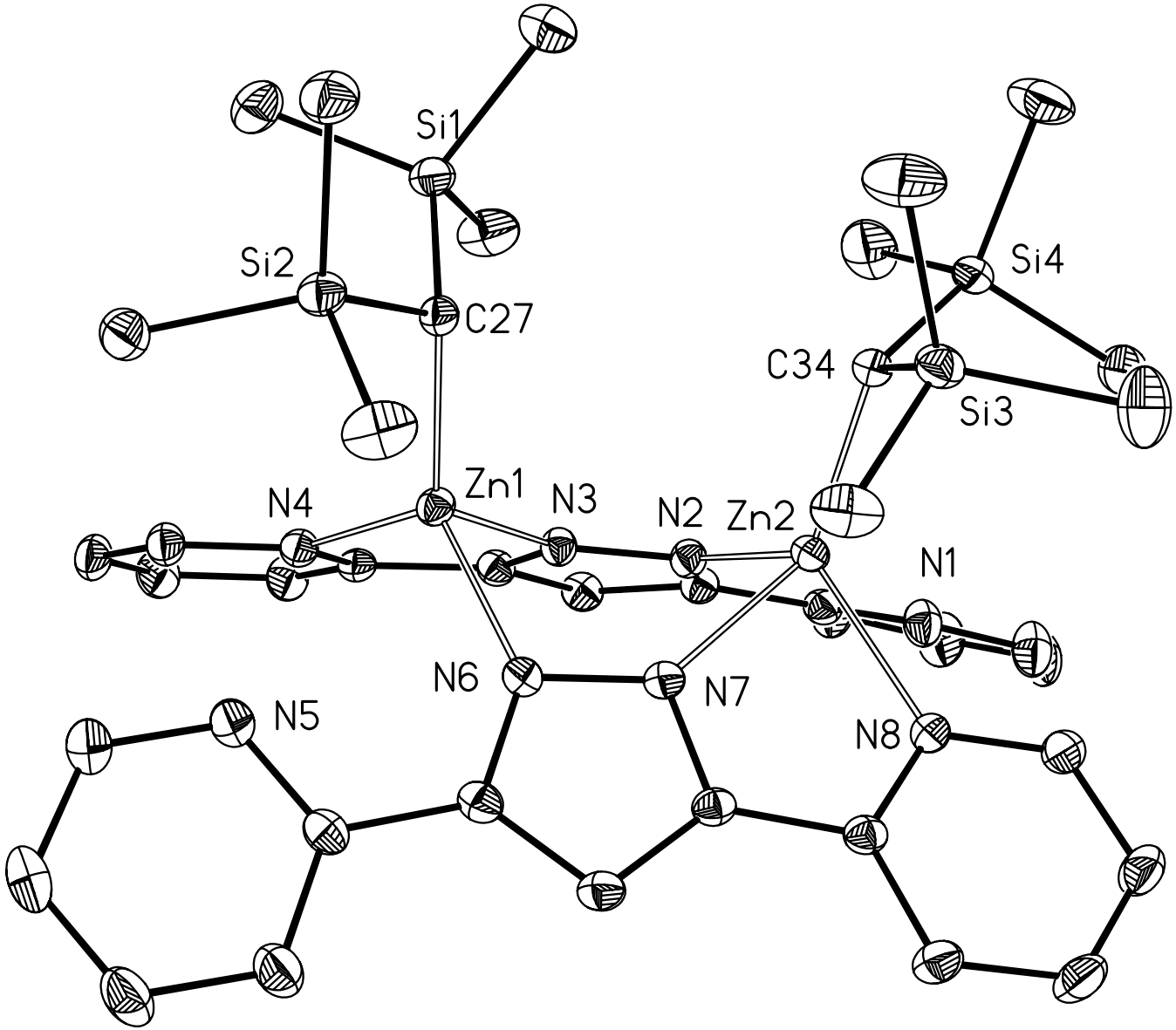

m+
N
M(L)n
N
N
M(L)n
N


m+
N
(L)n
M
N
N
N
N
N
M
(L)n
N
N



E = N (**1**), CH (**2**)


Si3
Si1
N10
Si2
N9
Si4
Zn2
N3
N2
Zn1
N4
N1
N5
N6
N7
N8


Si1
Si2
C27
Si4
C34
Si3
Zn1
N4
N3
N2
Zn2
N1
N6
N7
N5
N8