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# Lithium and Zinc Complexes of *C*- and *N*-Functionalized (2-Pyridylmethyl)amines

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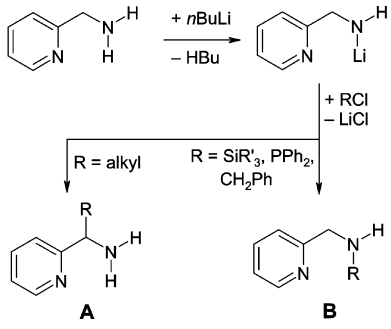
The addition reaction of benzophenone with lithium (2-pyridylmethyl)(*tert*-butyldimethylsilyl)amide yields dimeric 1-lithoxy-1,1-diphenyl-2-(2-pyridyl)-2-(trialkylsilylamino)ethane (**1**) with formation of a C–C bond. *C*-Functionalized 2-(pyridylmethyl)amines are accessible via the reaction of *N*-(2-pyridylmethylidene)phenylamine with diethylmalonate giving 2,2-bis(ethoxycarbonyl)-1-(phenylamino)-1-(2-pyridyl)ethane (**2**) which eliminates aniline upon heating yielding diethyl 2-(2-pyridylmethylidene)malonate (**3**). The addition of piperidine leads to the formation of the Michael type adduct 2,2-bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)-ethane (**4**) which can be deprotonated with metal-organic reagents such as $Zn[N(SiMe_3)_2]_2$, $Zn[CH(SiMe_3)_2]_2$, $LiN(SiMe_3)_2$, and $NaN(SiMe_3)_2$ leading to 2,2-bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)ethane-2-yl complexes of zinc (**5** and **6**), lithium (**7**), and sodium (**8**). *N*-Functionalization can be achieved via the reaction of (2-pyridylmethyl)(trialkylsilyl)amine with benzoyl chloride giving *N*-(2-pyridylmethyl)benzoylamine (**9**). Lithiation and subsequent salt metathesis reaction with another equivalent of benzoyl chloride yields *N*-(2-pyridylmethyl)dibenzoylamine (**10**). The addition reaction of $ZnCl_2$ with *N*-(2-pyridylmethyl)(diphenylmethylidene)amine (**11**) forms colorless crystalline [$(Py–CH_2N{=}CPh_2)ZnCl_2$] (**12**). The addition of benzoyl chloride leads to *N*-(diphenylchloromethyl)-*N*-(2-pyridylmethyl)benzoylamine (**13**). Addition of $ZnCl_2$ leads to the formation of solvent-separated [(2-pyridylmethyl)(benzoylamino)diphenylcarbonium] [(tetrahydrofuran)trichlorozincate] (**14**). The X-ray crystal structures of **1**, **4** to **7**, **9**, **12**, and **14** are discussed.



## Introduction

(2-Pyridylmethyl)amine and the substitution products represent a ligand of great interest due to the enormous biomimetic potential.[1,2] Therefore, the coordination behaviour of neutral (2-pyridylmethyl)amine towards zinc was extensively explored. This amino base acts as a bidentate ligand at zinc(II) cations, counterions being halide or pseudohalide anions.[3–9] Dialkylzinc deprotonates $Py–CH_2–NH_2$ at room temperature once and alkylzinc (2-pyridylmethyl)amide is formed quantitatively.[10] At elevated temperatures a second metallation step occurs and unintelligible reaction steps and degradation reactions follow. Therefore the amino group has to be protected which can easily be done by substitution of one H atom by a trialkylsilyl group according to Equation (1). Zincation of these (2-pyridylmethyl)(trialkylsilyl)amines yields the corresponding dimeric alkylzinc (2-pyridylmethyl)(trialkylsilyl)-amides.[11,12] Alkylation of (2-pyridylmethyl)amides yields *C*-alkylated picolylamines **A** which may also contain minor amounts of *N*-alkylation products **B** whereas phosphanylation occurs again only at the nitrogen atom [Equation (1)].[13]




(1)

Prolonged heating of alkylzinc (2-pyridylmethyl)(trialkylsilyl)amides in the presence of dialkylzinc leads to an oxidative C–C coupling of the picolylamides according to Equation (2).[11,12] van Koten and co-workers[14–17] prepared the di(*tert*-butyl)-protected 1,2-di(2-pyridyl)-1,2-diamidoethanes.These bis(alkylzinc) derivatives **C** dissociated in solution into radicals **D** via a homolytic C–C bond cleavage as shown in Equation (2). In the solid state only the dimer **C** was observed, however, the C–C bond length of the ethane backbone was extremely large. Protolysis of **C** (R as trialkylsilyl) with acetamide yields 1,2-dipyridyl-1,2-diaminoethane **E**[18] which can be again metallated with organometallic compounds.

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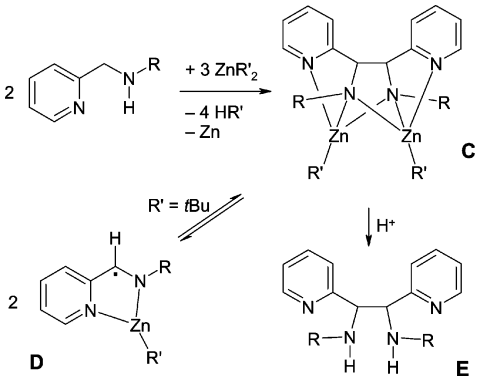
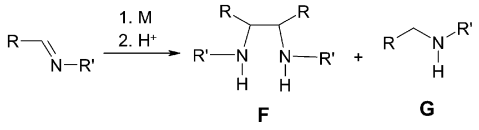


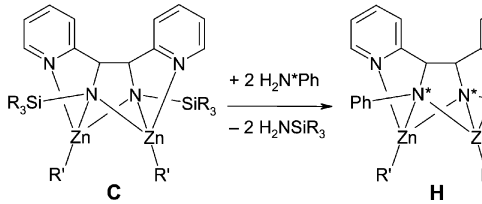

(2)

This oxidative C–C coupling of *N*-(trialkylsilyl)-protected picolylamines leads to $C_2$-symmetric complexes **C**. Another pathway offers the reductive C–C coupling of imines with metals (such as Zn/$Me_3SiCl$, Mg/$Me_3SiCl$, Al or Bi) to the 1,2-diaminoethanes **F** according to Equation (3), however, also minor amounts of reduction products, amines **G**, are formed occasionally.[19,20]




(3)

Metal complexes **C** with 1,2-dipyridyl-1,2-diamido ligands contain a folded $M_2N_2$ ring which leads to very small M···M contacts giving rise to an unusual chemistry as displayed in Equation (4). Whereas acetamide yields the protolysis product **E**, aniline gives rise to substitution product **H**.[18] Experiments with [$^{15}$N]aniline show that proton-transfer reactions lead to this unusual reaction behaviour and that not only the trialkylsilyl groups are replaced by phenyl substituents but the $NSiR_3$ units against NPh moieties.



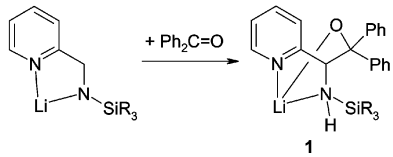

(4)

The oxidative C–C coupling of 2-pyridylmethylamines with organometallic compounds such as dimethylzinc or $Sn[N(SiMe_3)_2]_2$[11,12] as well as the reductive C–C coupling of imines[19,20] yield $C_2$-symmetric chelate Lewis bases. In order to develop unsymmetric tetradentate ligands which are able to form polynuclear complexes, other synthetic strategies have to be applied.

## Results and Discussion

### *Synthesis*

In order to obtain multi-dentate bases with an unsymmetric coordination sphere other reaction cascades were explored. *C*-Substitution of (2-pyridylmethyl)amine can be achieved by reaction of (2-pyridylmethyl)(trialkylsilyl)-amine with *n*-butyllithium giving [lithium (2-pyridylmethyl)(trialkylsilyl)amide][21] and thereafter with benzophenone yielding dimeric 1-lithoxy-1,1-diphenyl-2-(2-pyridyl)-2-(trialkylsilylamino)ethane (**1**) according to Equation (5). This compound is also accessible by reaction of doubly lithiated (2-pyridylmethyl)(trialkylsilyl)amine[21] with benzophenone and subsequent partial hydrolysis.[22] The solid-state structure of **1** was determined in order to clarify the coordination behaviour of this tridentate ligand.

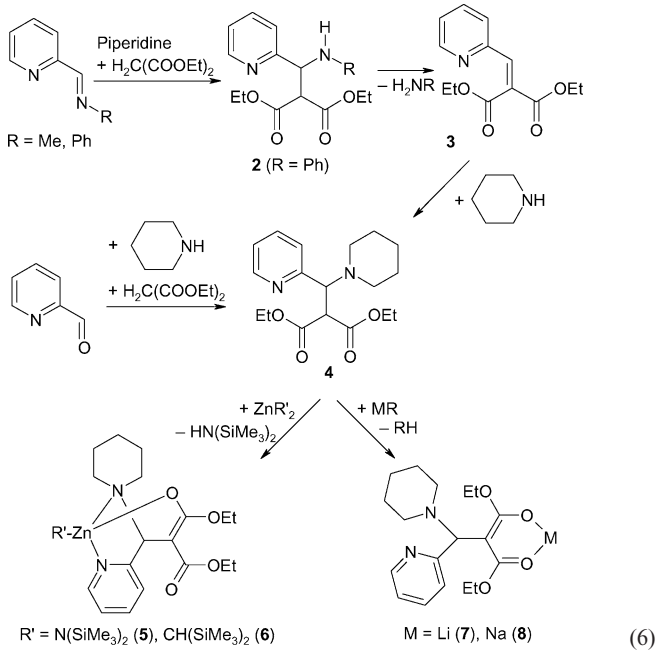



(5)

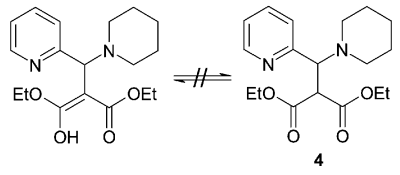
The base-catalyzed (e.g. piperidine) reaction of (2-pyridylmethylidene)(phenyl)amine with diethyl malonate yields 2,2-bis(ethoxycarbonyl)-1-(phenylamino)-1-(2-pyridyl)-ethane (**2**) according to a known procedure.[23] Compound **2** eliminates aniline upon heating to give the deamination product diethyl 2-(2-pyridylmethylidene)malonate (**3**). The use of *N*-(2-pyridylmethylidene)methylamine in this reaction leads to the formation of **3** without the observation of intermediate **2**. Very recently, **3** was also obtained in 1-butyl-3-methylimidazolium hydroxide [bmim]OH which functions as a solvent as well as a catalyst for the Knoevenagel condensation.[24] Bromomalonic esters also proved to be suitable starting materials in order to prepare **3**.[25,26] The addition of piperidine to compound **3** yields the Michael type adduct 2,2-bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)ethane (**4**). This reaction sequence is shown in Equation (6). Similar procedures, namely the addition of diethylamine to diethyl [(3-nitro-2-pyridyl)methylidene]malonate[27] as well as of piperidine to diethyl 2-(2-nitrobenzylidene)malonate,[28] were reported by Kinastowski, Wnuk and others. Compound **4** is also accessible via the reaction of pyridine-2-carbaldehyde with diethyl malonate in the presence of a stoichiometric amount of piperidine.

Compound **4** shows no keto-enol tautomerism in the NMR experiments [Equation (7)]. Furthermore, no H/D exchange is observed after addition of [$D_4$]methanol to solutions of **4**. Nevertheless, this derivative is easily deprotonated. The metallation of **4** with zinc bis[bis(trimethylsilyl)amide] gives the monomeric complex **5** with a tridentate ligand, which binds with both nitrogen atoms and one oxygen base to the cation. Alkali metal bis(trimethylsilyl)-amides are also suitable metallation reagents. Sodium derivative **8** is only sparingly soluble in common organic solvents which can be understood in the sense of a mainly ionic salt-like complex.



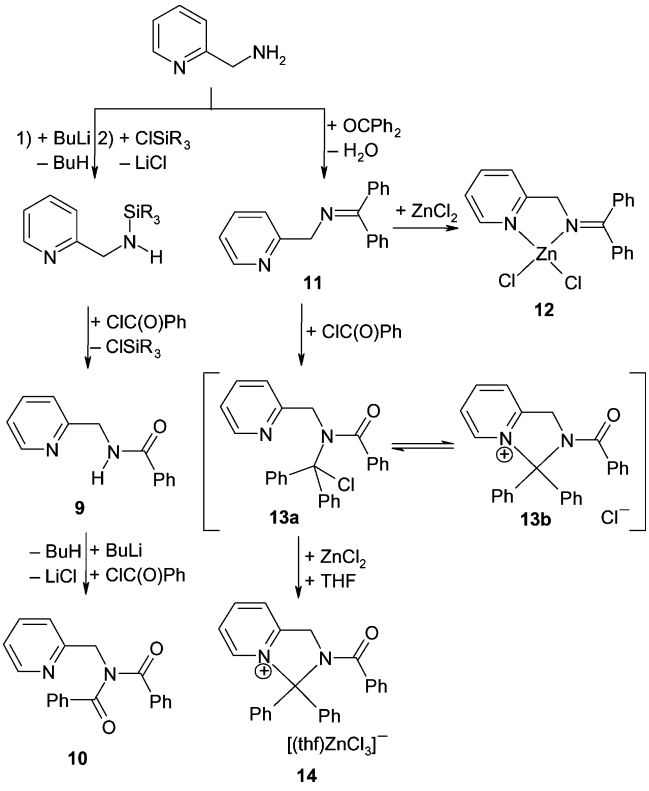

(6)




(7)

*N*-Functionalization of (2-pyridylmethyl)amines with moieties which contain Lewis bases with oxygen-donor atoms is known for acylation reactions. *N*-acyl(2-pyridylmethyl)amines are valuable ligands which were recently investigated e.g. by Houser and co-workers.[29] The reaction of (2-pyridylmethyl)(trialkylsilyl)amines with benzoyl chlorides quantitatively yields *N*-(2-pyridylmethyl)benzoylamine (**9**). In order to obtain a tetradentate base, a second reaction cascade consisting of lithiation and subsequent salt metathesis reaction with benzoyl chloride according to Equation (8) was applied to give *N*-(2-pyridylmethyl)dibenzoylamine (**10**) in poor yield. This oily compound always contained traces of **9**. In order to further investigate the *N*-acylation another protecting group was chosen and *N*-(2-pyridylmethyl)(diphenylmethylidene)amine (**11**)[30] was employed as starting material. The coordination behaviour of this bidentate base is comparable to (2-pyridylmethyl)amine and addition of $ZnCl_2$ yields colorless crystalline [(Py–$CH_2N{=}CPh_2$)$ZnCl_2$] (**12**). However, addition of benzoyl chloride leads to compound **13a** with the benzoyl moiety bound again to the amine functionality according to Equation (8). Addition of $ZnCl_2$ leads to the formation of solvent-separated **14** with the $[(thf)ZnCl_3]^-$ anion. The similarity of the NMR spectroscopic data suggests that **13b** also might be an ion pair as displayed in Equation (8).

The $^{13}C\{^1H\}$ NMR spectroscopic data of *N*-(2-pyridylmethyl)(diphenylmethylidene)amine and of the acylation products are listed in Table 1. A general numbering scheme of these compounds is shown in Scheme 1.

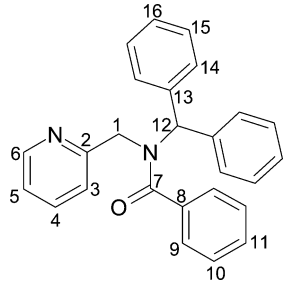



(8)

Table 1. Comparison of the $^{13}C\{^1H\}$ NMR shifts ($\delta$ values, ppm) of compounds **9**–**14**. The numbering scheme is given in Scheme 1.

| | **9** | **10** | **11** | **12** | **13** | **14** |
|---|---|---|---|---|---|---|
| C1 | 44.7 | 51.1 | 44.1 | 56.5 | 53.5 | 52.3 |
| C2 | 156.3 | 156.2 | 153.4 | 155.2 | 151.8 | 150.5 |
| C3 | 122.0 | 121.5 | 124.1 | 123.2 | 126.0 | 128.4 |
| C4 | 136.7 | 136.4 | 138.8 | 141.1 | 147.7 | 147.0 |
| C5 | 122.3 | 121.9 | 124.6 | 125.2 | 127.1 | 127.2 |
| C6 | 148.8 | 148.9 | 150.0 | 148.1 | 138.0 | 138.3 |
| C7 | 167.3 | 170.8/173.9 | – | – | 168.0 | 168.0 |
| C8 | 134.2 | 136.1 | – | – | [a] | [a] |
| C9 | 127.0 | 127.8/128.1 | – | – | [a] | [a] |
| C10 | 125.4 | 129.2/129.8 | – | – | [a] | [a] |
| C11 | 131.3 | 131.4/133.2 | – | – | [a] | [a] |
| C12 | – | – | 196.7 | 181.6 | 97.4 | 96.8 |
| C13 | – | – | 138.5 | 135.8/138.5 | [a] | [a] |
| C14 | – | – | 130.6 | 127.6/130.0 | [a] | [a] |
| C15 | – | – | 129.2 | 129.2/129.8 | [a] | [a] |
| C16 | – | – | 133.4 | 131.1/133.1 | [a] | [a] |

[a] Assignment was not possible.



Scheme 1. Numbering scheme for the assignment of the NMR parameters of compounds **9**–**14**.

### *Molecular Structures*

The molecular structure of 1-lithoxy-1,1-diphenyl-2-(2-pyridyl)-2-(trialkylsilylamino)ethane (**1**) is shown in Figure 1. Atoms generated by inversion symmetry ($-x + 1$, $-y + 2$, $-z$) are marked with an "A". The atom N2 is chiral, however, due to the inversion symmetry a racemate is obtained. All three Lewis bases coordinate to the lithium atom giving a tridentate ligand. This complex dimerizes via a $Li_2O_2$ ring yielding a strongly distorted tetrahedral environment of the lithium atoms. Dimerization of lithium derivatives via formation of $Li_2O_2$ rings is a common behaviour for alcoholates and related compounds (e.g. ref.[31,32]). The proton binds to the silylated amino group at N2 and shows no involvement in any hydrogen bridges. The N2–Si bond of 175.0(3) pm is rather long due to the tetracoordinated nitrogen atom which prevents an effective hyperconjugation and backdonation of charge to the trialkylsilyl group.

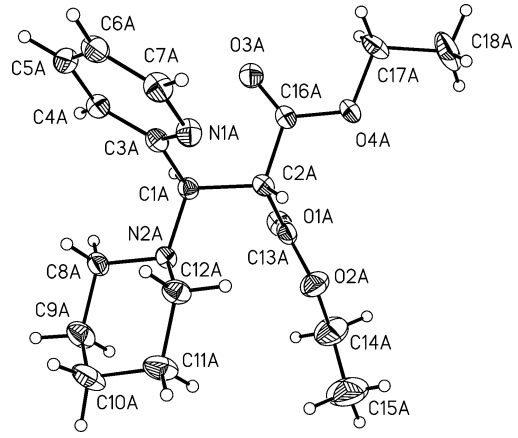



Figure 2. Molecular structure and numbering scheme of 1-(2-pyridyl)-1-piperidyl-2,2-bis(ethoxycarbonyl)ethane (**4**). The ellipsoids represent a probability of 40%, H atoms are shown with arbitrary radii.

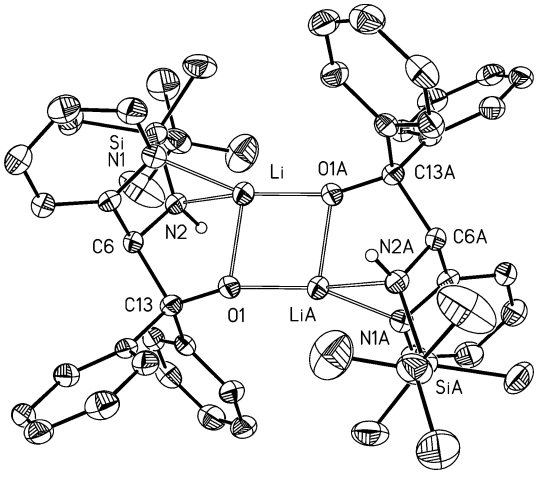



Figure 1. Molecular structure and numbering scheme of dimeric 1-lithoxy-1,1-diphenyl-2-(2-pyridyl)-2-(trialkylsilylamino)ethane (**1**). The ellipsoids represent a probability of 40%. Hydrogen atoms with the exception of the NH fragment are omitted for clarity reasons.

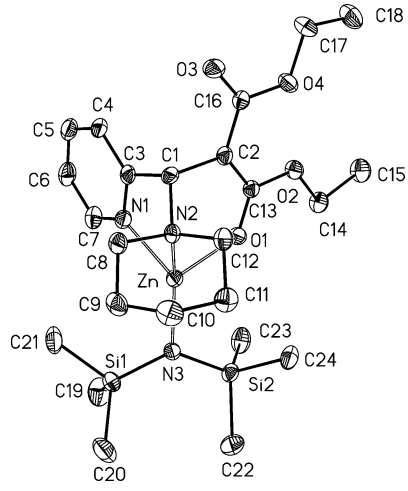



Figure 3. Molecular structure and numbering scheme of bis(trimethylsilyl)amidozinc 2,2-bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)ethan-2-ide (**5**). The ellipsoids represent a probability of 40%, hydrogen atoms are neglected for the sake of clarity.

The ligand shows an extremely large C6–C13 bond length of 158.4(4) pm. Similar values were also observed for metallated 1,2-diamino-1,2-dipyridylethanes.[11,12] This observation can be explained by electrostatic repulsion between carbon atoms with a similar charge due to comparable inductive and mesomeric effects of the substituents at C6 and C13.

The molecular structures of **4**, **5** and **6** are represented in Figure 2, Figure 3 and Figure 4, respectively. The numbering schemes are identical in order to allow a direct comparison of the structural data. Compound **4** crystallizes with two symmetry independent molecules in the asymmetric unit distinguished by the letters "A" and "B". In Table 2 selected structural parameters of these compounds are listed. The metallation of **4** leads to a deprotonation at C2 which allows the formation of a β-diketonate with a delocalized charge within the O1–C13–C2–C16–O3 moiety.

Several features result from a comparison of neutral **4** and its metallated derivatives **5**, **6** and **7**: (i) The bond lengths of the pyridyl unit are not affected by the coordination to lithium (**7**) and zinc (**5** and **6**). (ii) The coordination of the piperidyl group to the metal atoms leads to an elongation of the bonds to N2. However, in all molecules a chair conformation is adopted. (iii) The shortening of the C1–C2 bond is a consequence of the increased s-orbital participation at C2 ($sp^2$ hybridization in **5**, **6** and **7** vs. $sp^3$ in **4**) in the metallated derivatives. (iv) Due to the deprotonation a planar environment at C2 is realized. The anionic charge is delocalized throughout the O1–C13–C2–C16–O3 unit yielding elongated C13–O1 and C16–O3 bonds and shortened C2–C13 as well as C2–C16 bonds. In addition this unit is planarily arranged whereas in **4** the planar ester functions are distorted in order to minimize steric repulsive forces. The coordination of zinc to O1 enhances the nega-

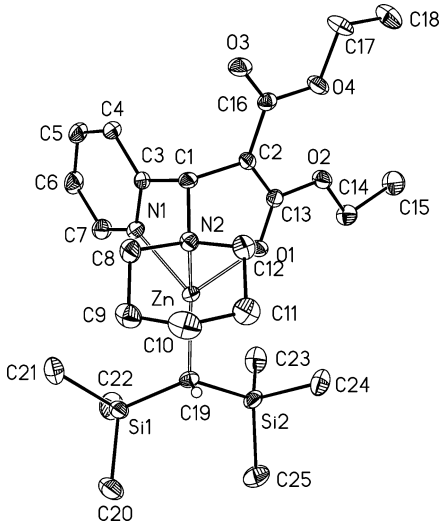



Figure 4. Molecular structure and numbering scheme of bis(trimethylsilyl)methylzinc 2,2-bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)ethan-2-ide (**6**). The ellipsoids represent a probability of 40%. H atoms are omitted for clarity reasons with the exception of the zinc-bound methyl group.

Table 2. Comparison of the structural parameters of **4** (molecules A and B), **5**, **6**, and **7**. For **7** average values are given; selected structural parameters are listed in Table 2.

| | **4A** | **4B** | **5** | **6** | **7**[a] |
|---|---|---|---|---|---|
| C1–C2 | 153.0(3) | 153.4(3) | 151.8(4) | 151.9(3) | 150.7 |
| C1–C3 | 152.5(4) | 151.3(3) | 151.3(4) | 151.1(3) | 151.7 |
| C1–N2 | 147.8(3) | 148.2(3) | 150.8(3) | 150.6(3) | 150.3 |
| N2–C8 | 146.6(3) | 146.3(3) | 149.4(3) | 149.2(3) | 148.0 |
| N2–C12 | 147.5(3) | 146.5(3) | 148.4(3) | 148.6(3) | 147.2 |
| C3–C4 | 138.7(4) | 139.3(4) | 139.7(4) | 139.6(3) | 138.9 |
| C4–C5 | 138.4(4) | 138.7(4) | 137.3(4) | 137.3(4) | 138.0 |
| C5–C6 | 138.4(4) | 137.7(4) | 137.6(5) | 139.0(4) | 137.9 |
| C6–C7 | 137.7(4) | 138.0(4) | 138.3(4) | 137.7(3) | 137.3 |
| N1–C3 | 134.2(3) | 134.4(3) | 134.6(3) | 134.7(3) | 133.7 |
| N1–C7 | 134.0(4) | 134.0(4) | 133.9(3) | 134.2(3) | 133.7 |
| C2–C13 | 152.1(4) | 151.9(4) | 139.7(4) | 139.6(3) | 141.6 |
| C13–O1 | 120.5(3) | 120.8(3) | 127.2(3) | 127.0(3) | 123.4 |
| O2–C13 | 132.2(3) | 132.4(3) | 134.3(3) | 134.3(3) | 137.2 |
| O2–C14 | 146.6(4) | 145.8(4) | 144.3(3) | 144.0(3) | 143.8 |
| C2–C16 | 152.3(3) | 152.6(3) | 144.5(4) | 144.5(3) | 141.9 |
| C16–O3 | 119.2(3) | 119.2(3) | 123.1(3) | 122.4(3) | 123.7 |
| O4–C16 | 133.5(3) | 133.4(3) | 134.7(3) | 134.7(3) | 136.6 |
| O4–C17 | 146.8(3) | 146.1(3) | 143.5(3) | 144.0(3) | 144.0 |
| M–N1 | – | – | 206.4(2) | 207.6(2) | 213.6 |
| M–N2 | – | – | 211.4(2) | 213.9(2) | 217.7 |
| M–O1 | – | – | 199.8(2) | 200.7(2) | 195.3 |
| M–O2 | – | – | – | – | 233.0 |
| M–O3 | – | – | – | – | 194.5 |
| M–N3/C19 | – | – | 189.3(2) | 198.0(2) | – |
| N3/C19–Si1 | – | – | 171.5(2) | 185.2(2) | – |
| N3/C19–Si2 | – | – | 171.6(2) | 185.1(2) | – |

[a] Average values.

tive charge and the coordination number of this oxygen atom yielding larger C13–O1 distances than C16–O3 values.

The Zn–N3 bond length to the bis(trimethylsilyl)amido group shows a value of 189.3(2) pm which is larger than observed for homoleptic $Zn[N(SiMe_3)_2]_2$ with a two-coordinate zinc atom [X-ray diffraction, solid state: 183(1) pm;[33] electron diffraction, gas phase: 182(1) pm[34]]. Enhancement of the coordination number to three in $[(Me_3Si)_2N–Zn(\mu\text{-}OCEt_3)]_2$ gives Zn–N bonds lengths of 186.8(3) pm.[35] A further enhancement of the coordination number of zinc as, for example, in monomeric $Zn\{N(2,6\text{-}iPr_2H_3C_6)–SiMe_2–NMe_2\}_2$[36] and $Zn\{N(SiMe_3)CH_2CH_2NMe_2\}_2$[37] with a tetra-coordinate metal center leads to increased Zn–N distances comparable to those of **5**. Furthermore, an enhanced electrostatic repulsion between three anionic groups was observed in solvent-separated zincates with $[Zn\{N(SiMe_3)_2\}_3]^-$ anions leading to rather large Zn–N distances.[38,39] The distances of the coordinative Zn–N1 and Zn–N2 bonds to the pyridyl and piperidyl groups are much larger due to a reduced electrostatic attraction. Steric strain leads to a rather large Si1–N3–Si2 angle of 125.3(1)° at a nearly planar N3 atom (angle sum 357.8°). The dependency of the Si–N–Si angles in bis(trimethylsilyl)amides of the Si–N bond lengths (and hence of the electronegativity of the metal) was discussed by Hanusa and co-workers.[40]

The lithium derivative **7** crystallizes as a tetramer as shown in Figure 5. The four monomers are distinguished by the letters "A" to "D". The large gaps between these molecules contain solvent molecules (toluene, pentane) which are heavily disordered thus hampering the quality of the structure determination. However, the framework formed by compound **7** shows no thermal motion and, hence, rather small e.s.d. values. The smallest unit can be interpreted as a lithium β-diketonate derivative with the lithium atom in a bridging position between the oxygen atoms O1 and O3. In Table 3 the bond lengths of the four units are listed. The organic anions show very similar structural parameters. However, strong differences are observed for the LiX–O2(X+1) bonds. The LiB–O2C distance exhibits a value of 256.2(6) pm and is much larger than the corresponding values of the other lithium atoms. The C–O single

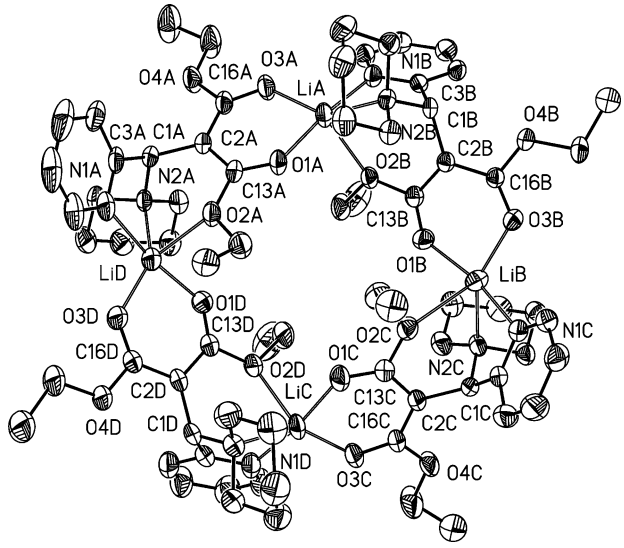



Figure 5. Molecular structure and numbering scheme of tetrameric lithium 2,2-bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)ethan-2-ide (**7**). The ellipsoids represent a probability of 40%; H atoms are neglected for clarity reasons.

bonds of **7** are rather small compared to standard values. This fact can be attributed to an additional electrostatic attraction as a consequence of a highly positive carbon atom. Similar observations are discussed in detail by Becker et al.[41] for sesqui(1,2-dimethoxyethane)lithium bis(methoxycarbonyl)phosphanide.

Table 3. Selected structural parameters of tetrameric **7**. The four molecules are distinguished by the letters X = A, B, C, and D. The letter (X + 1) shows that this coordination is carried out to the neighbouring molecule (A + 1 = B, B + 1 = C, C + 1 = D, D + 1 = A). Selected structural parameters are listed in Table 4.

| X | A | B | C | D |
|---|---|---|---|---|
| LiX–O1X | 195.9(5) | 193.9(6) | 195.8(7) | 195.6(6) |
| LiX–O3X | 197.0(6) | 196.4(6) | 193.0(6) | 191.3(6) |
| LiX–O2(X + 1) | 224.0(6) | 256.2(6) | 223.7(7) | 227.2(6) |
| LiX–N1(X + 1) | 212.0(6) | 209.1(6) | 213.8(7) | 213.3(6) |
| LiX–N2(X + 1) | 219.9(6) | 218.0(6) | 216.4(6) | 217.8(6) |
| O1X–C13X | 123.6(3) | 123.6(4) | 124.0(4) | 122.4(4) |
| C2X–C13X | 141.0(4) | 141.5(4) | 141.4(4) | 141.7(4) |
| C2X–C16X | 141.7(4) | 142.0(4) | 141.6(5) | 142.1(5) |
| O3X–C16X | 123.6(4) | 123.6(4) | 123.7(4) | 123.4(4) |
| C1X–C2X | 151.3(4) | 151.7(4) | 150.3(4) | 149.8(5) |
| O2X–C13X | 137.7(4) | 137.5(4) | 136.2(4) | 138.2(4) |
| O2X–C14X | 143.1(4) | 144.1(4) | 143.6(4) | 144.7(4) |
| O4X–C16X | 137.9(4) | 136.1(4) | 136.6(4) | 136.2(4) |
| O4X–C17X | 144.0(5) | 143.5(4) | 142.6(5) | 144.0(5) |

The molecular structure of *N*-(2-pyridylmethyl)benzoylamine (**9**) is shown in Figure 6. The two crystallographically independent molecules are distinguished by the letters "A" and "B". The hydrogen atoms were located and the amine nitrogen N2 is in a planar environment (angle sums 359.6° and 359.9°). Weak N–H···O hydrogen bridges lead to a strand formation in the solid state. The C7–O1 bond lengths of 123.7(2) and 124.1(2) pm are slightly elongated in comparison to isolated C=O double bonds. The values of the N2–C7 bond lengths of 133.9(2) and 133.5(2) pm show the formation of allylic O1–C7–N2 systems (3-center 4-electron π-system) and are very similar to the N1–C1 [133.9(3) and 133.5(3) pm] and N1–C5 [133.9(2) and 134.5(2) pm] distances of the pyridyl group. A further delocalization of charge from this allylic system into the phenyl fragment does not occur and can be deduced from characteristic C7–C8 single bonds of 149.8(2) and 149.6(2) pm.

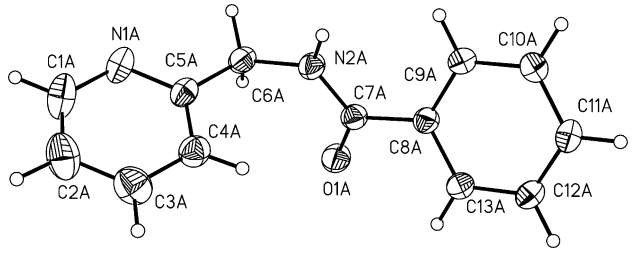



Figure 6. Molecular structure and numbering scheme of *N*-(2-pyridylmethyl)benzoylamine (**9**). The ellipsoids represent a probability of 40%; H atoms are shown with arbitrary radii.

The coordination behaviour of *N*-(2-pyridylmethyl)benzoylamine (**9**) to copper(I) chloride was already investigated. Yang and Houser[29c] showed that only the pyridyl base of **9** acts as a coordination site towards copper(I). The crystal structures of copper(I) complexes with *N*-(2-pyridylmethyl)acetylamine are also influenced by intermolecular hydrogen bridges of the NH···O type, whereas the chloride counterions bridge two copper cations.

The molecular structure of **12** is shown in Figure 7. The zinc atom is in a distorted tetrahedral environment. Molecules with an 2-[(alkylideneamino)methyl]pyridine ligand at zinc are already well-known.[9,42] The small bite of the ligand leads to a small N1–Zn–N2 bond angle of 81.53(7)°, the Zn–N bond lengths lying in a characteristic range.[9] This small angle allows a Cl1–Zn–Cl2 angle of 117.39(3)°.

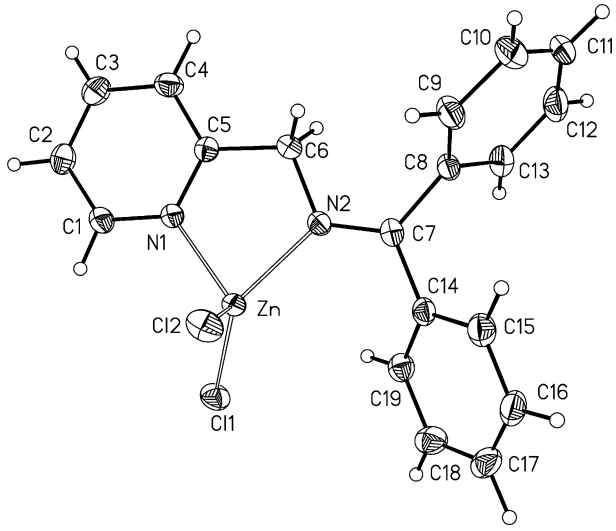



Figure 7. Molecular structure and numbering scheme of [(diphenylmethylidene)(2-pyridylmethyl)amino]zinc(II) chloride (**12**). The ellipsoids represent a probability of 40%. The H atoms are drawn with arbitrary radii.

Compound **14** crystallizes as a solvent-separated ion pair, shown in Figure 8. The anion $[(thf)ZnCl_3]^-$ with the metal center in a distorted tetrahedral environment is already well-known and a common counterion in many complexes.[43] The Zn–Cl bond lengths are only slightly larger than observed for **12** which might be the consequence of intramolecular electrostatic repulsion between the chlorine anions.

The organic cation consists of the (benzoyl)(2-pyridylmethyl)amino unit with a diphenylmethyl cation at N2 which also binds to the pyridyl base N1. Both nitrogen bases are in nearly planar environments. The N2–C1 and N2–C2 bond lengths adopt characteristic values for N–C single bonds whereas the N2–C8 distance is approximately 10 pm smaller. This fact supports the formation of an allylic π-system as described for *N*-(2-pyridylmethyl)benzoylamine (**9**). Due to ring strain the bonding between the diphenylmethyl cation and the pyridyl base [N1–C1 151.9(4)] is slightly larger than the other bond lengths. However, this bond does not affect the delocalization within the pyridyl fragment.

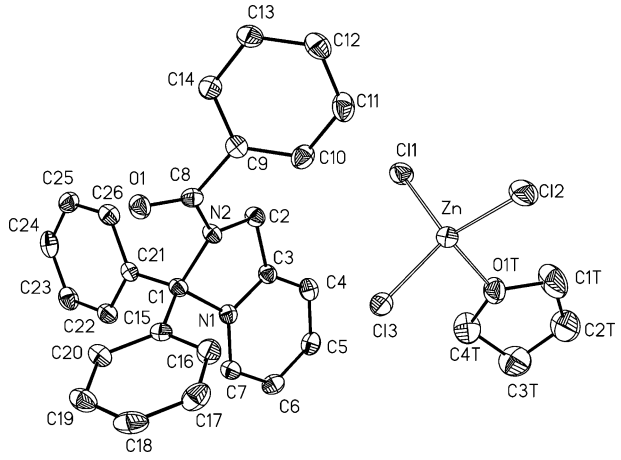
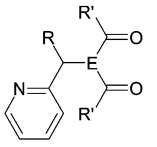



Figure 8. Molecular structure andnumbering scheme of zincate **14**. The ellipsoids represent a probability of 40%, H atoms are omitted for clarity reasons.

## Conclusions

We are interested in multidentate Lewis bases containing the (2-pyridylmethyl)amino unit. Two compound classes fulfil these conditions, namely the derivatives of diethyl malonate (E = $C^-$) with the negative charge delocalized within the 1,3-diketonate fragment as well as *N*-benzoyl-substituted (2-pyridylmethyl)amines (E = N).




E = $C^-$
R = N(H)Ph (**2**), $N(CH_2)_5$ (**4**)
R' = OEt

E = N
R = H (**9**)
R' = phenyl

The deprotonation of **4** yields the corresponding zinc (**5** and **6**), lithium (**7**) and sodium (**8**) derivatives. This ligand binds to zinc in a tridentate manner via both the nitrogen bases and one keto group whereas the lithium cation is bound to the β-diketonate moiety; an intermolecular coordination to the nitrogen bases of the neighbouring molecule leads to the formation of cyclic tetramers. This fact can be explained with the Pearson concept of hard/soft acids and bases.[44] Whereas the soft 3d-element zinc binds to the softer nitrogen bases, the hard lithium cation prefers the negatively charged β-diketonate moiety. The sodium derivative is only sparingly soluble in common organic solvents and therefore, recrystallization fails. However, the insolubility supports the assumption that a polymeric strand structure is formed.

The *N*-(2-pyridylmethyl)dibenzoylamines are formed via an acylation of (2-pyridylmethyl)amine. Despite a protection of the amine function with the diphenylmethylidene fragment, benzoyl chloride attacks the imino nitrogen base and binds to both of the nitrogen atoms, thus forming a five-membered heterocycle. Products of *C*-acylation reactions were not observed. Zinc(II) chloride reacts as a Lewis acid and hence, addition of zinc(II) chloride yields a solvent-separated ion pair with the already well-known [(thf)-$ZnCl_3$]$^-$ anion.

## Experimental Section

**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. Starting **11** was prepared in analogy to a published procedure.[45] $^1$H and $^{13}$C NMR spectra were recorded at ambient temperature on a Bruker AC 200 or a Bruker AC 400 spectrometer. DEI-mass spectra were obtained on a Finnigan MAT SSQ 710 system, 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.

**2-(*tert*-Butyldimethylsilylamino)-1-lithoxy-1,1-diphenyl-2-(2-pyridyl)-ethane (1):** A 1.6 M solution of *n*-butyllithium in hexane (1.6 M, 5.1 mL, 8.2 mmol) was dropped at –78 °C to a solution of 1.83 g of (*tert*-butyldimethylsilyl)(2-pyridylmethyl)amine (8.2 mmol) in 5 mL of toluene. Thereafter, 1.49 g of benzophenone (8.2 mmol) in 5 mL of toluene were added dropwise at –78 °C. After complete addition, the reaction mixture was warmed to room temp. and stirred for additional 50 h. Then all volatile components were removed at room temp. under vacuum and the residue was redissolved in 7.5 mL of toluene and tempered at 75 °C for 4 h. After removal of all solids, storage at r.t. afforded 0.9 g of colorless crystalline **1** (2.2 mmol, 27%). $^1$H NMR ($CDCl_3$): $\delta$ = 8.31 (s, 1 H, br, Py1), 7.6–6.8 (13 H, Ph2–Ph4, Py2–Py4), 4.70 (d, $^3J$ = 5 Hz, 1 H, C6, CH), 1.80 (d, $^3J$ = 5.6 Hz, 1 H, C–NH–Si),0.58 (s, 9 H, Si–$CMe_3$), –0.33 and –0.350 (6 H, Si–$CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 148.4 (Py1), 147.1 (Ph, $C_q$), 145.7 (Ph, $C_q$), 136.5 (Py3), 132.4–126.2 (Ph), $\delta$ = 123.6 (Py4), 121.5 (Py2), 81.8 (C7), 61.8 (C6, CH), 26.0 [Si–C($CH_3$)$_3$], 17.7 (Si–$CMe_3$), –4.8 ($SiMe_2$) ppm. IR (Nujol, $cm^{-1}$): $\tilde{\nu}$ = 3362 (m), 3058 (w), 1597 (s), 1571 (m), 1377 (vs), 1335 (w), 1256 (m), 1248 (m), 1186 (w), 1162 (w), 1130 (m), 1078 (s), 1063 (w), 1048 (w), 967 (w), 945 (m), 905 (w), 862 (m), 856 (m), 836 (s), 830 (s), 812 (w), 774 (s), 751 (s), 706 (vs), 701 (vs), 662 (w), 644 (w), 636 (w), 609 (w), 571 (w), 531 (w), 487 (w) $cm^{-1}$. MS: *m*/*z* (%) = 821 (19) [$M^+$ of dimer], 639 (6) [$C_{37}H_{50}Li_2N_4OSi_2$], 410 (9) [monomer], 387 (54) [$C_{25}H_{31}N_2Si$], 221 (99) [$C_{12}H_{21}N_2Si$ + H], 182 (98) [$C_{13}H_{10}O$], 164 (98) [$C_8H_{12}N_2Si$ + H], 105 (86) [$C_6H_5N_2$], 77 (70) [$C_6H_5$], 73 (41) [$C_2H_7NSi$ + H], 57 (25) [Bu]. $C_{25}H_{31}Li_2N_2OSi$ (416.49): calcd. C 72.10, H 7.26, N 6.73; found C 72.55, H 7.29, N 6.20.

**2,2-Bis(ethoxycarbonyl)-1-phenylamino-1-(2-pyridyl)ethane (2):** A mixture of 1.03 g of 2-(phenyliminomethyl)pyridine (5.56 mmol), 1.36 g of diethyl malonate (8.48 mmol) and 0.2 mL of piperidine were stirred for 6 days at room temp. After removal of piperidine a waxy dark brown oil remained and 15 mL of heptane were added. Thereupon, 1.34 g of a colorless solid of **2** (3.91 mmol, 70%) formed, which was collected, washed with a small amount of heptane and dried in vacuo; m.p. 72.5 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 8.51 [d, $^3J$(H,H) = 4.8 Hz, 1 H, Pyr1], 7.55 [dt, $^3J$(H,H) = 7.6, $^5J$(H,H) = 1.6 Hz, 1 H, Pyr3], 7.36 [d, $^3J$(H,H) = 7.6 Hz, 1 H, Pyr4], 7.11 (m, 3 H, Pyr2, Ph3/3′), 6.67 (m, 3 H, Ph2/2′,4), 5.32 (m, 1 H, CHN), 5.16 [d, $^3J$(H,H) = 10.0 Hz, 1 H, NH], 4.37 [d, $^3J$(H,H) = 6.0 Hz, 1 H, $CH(COOEt)_2$], 4.08 (m, 4 H, $OCH_2$), 1.13 (m, 6 H, $CH_3$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ = 168.4 (C=O), $\delta$ = 167.8 (C=O), 159.5 (Pyr5), $\delta$ = 149.2 (Pyr1), 146.9 (Ph1), 136.5 (Pyr3), 129.2 (Ph3/3′), 122.3 (Pyr2), 122.0 (Pyr4), 118.1 (Ph4), 113.5 (Ph2/2′), 61.6 ($OCH_2$), 61.4 (O′$CH_2$), 58.3 (CHN), 56.3 [$CH(COOEt)_2$], 13.9 ($CH_3$) ppm. IR (Nujol, $cm^{-1}$): $\tilde{\nu}$ = 3283 (s), 3064 (m), 2925 (vs), 2854 (vs), 1753 (vs), 1604 (s), 1593 (s), 1570 (m), 1527 (m), 1501 (s), 1462 (vs), 1369 (s), 1311 (vs), 1287 (s), 1271 (vs), 1216 (m), 1192 (m), 1178 (s), 1133 (vs), 1094 (m), 1028 (s), 997 (m), 887

(m), 790 (m), 757 (s), 694 (s), 621 (w), 605 (m), 561 (w), 519 (w) $cm^{-1}$. $C_{19}H_{22}N_2O_4$ (342.38): calcd. C 66.66, H 6.46, N 8.03; found C 66.65, H 6.48, N 8.18.

**2,2-Bis(ethoxycarbonyl)-1-piperidyl-1-(2-pyridyl)ethane (4):** A mixture of 1.07 g of pyridine-2-carbaldehyde (10.0 mmol), 1.92 g of diethyl malonate (12.0 mmol) and 1.02 g of piperidine (12.0 mmol) was dissolved in 20 mL of anhydrous ethanol and heated under reflux for 3 h. After removal of the solvent at room temp. in vacuo, the dark-brown oil was dissolved in 5 mL of ethyl acetate and 25 mL of hexane. The volume was reduced to half of the original volume. From this solution 1.98 g of colorless prisms of **4** (5.92 mmol, 59%) precipitated and were collected, washed with pentane and dried under vacuum; m.p. 68.5 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 8.50 [d, $^3J$(H,H) = 4.4 Hz, 1 H, Pyr1], 7.61 [dt, $^3J$(H,H) = 7.6, $^5J$(H,H) = 1.6 Hz, 1 H, Pyr3], 7.14 [d, $^3J$(H,H) = 7.6 Hz, 1 H, Pyr4], 7.12 (m, 1 H, Pyr2), 4.66 [d, $^3J$(H,H) = 11.6 Hz, 1 H, $CH(COOEt)_2$], 4.40 [d, $^3J$(H,H) = 11.6 Hz, 1 H, CHN], 4.24 (m, 2 H, $OCH_2$), 3.98 (m, 2 H, O′$CH_2$), 2.61 (m, 2 H, Pip2), 2.11 (m, 2 H, Pip2′), 1.43 (m, 4 H, Pip3/3′), 1.32 [t, $^3J$(H,H) = 7.2 Hz, 3 H, $CH_3$], 1.13 (m, 2 H, Pip4), 1.13 [t, $^3J$(H,H) = 7.2 Hz, 3 H, ′$CH_3$] ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 168.7 (C=O), 168.0 (′C=O), 155.5 (Pyr5), 148.6 (Pyr1), 135.6 (Pyr3), 124.2 (Pyr4), 122.1 (Pyr2), 69.1 (CHN), 61.1 ($OCH_2$), 60.9 (O′$CH_2$), 53.7 [$CH(COOEt)_2$], 50.9 (Pip2/2′), 26.6 (Pip3/3′), 24.5 (Pip4), 14.3 ($CH_3$), 13.8 (′$CH_3$) ppm. IR (Nujol, $cm^{-1}$): $\tilde{\nu}$ = 3444 (m), 2921 (vs), 2854 (vs), 2729 (m), 1741 (vs), 1721 (s), 1590 (m), 1568 (m), 1463 (vs), 1376 (s), 1300 (s), 1267 (s), 1241 (m), 1227 (m), 1181 (m), 1157 (s), 1112 (m), 1095 (m), 1035 (s), 1020 (s), 995 (m), 888 (m), 813 (m), 756 (m), 722 (m), 621 (w), 551 (w) $cm^{-1}$. MS (DEI): *m/z* (%) = 335 (13) $[MH]^+$, 251 (100) $[MH^+ - C_5H_{10}N]$, 178 (90) $[(C_{10}H_{12}NO_2)^+]$, 132 (84) $[C_8H_6NO]^+$, 84 (55) $[C_5H_{10}N]^+$, 78 (14) $[C_5H_4N]^+$. $C_{18}H_{26}N_2O_4$ (334.41): calcd. C 64.65, H 7.48, N 8.59; found C 64.83, H 8.05, N 8.39.

**[3-(2-Pyridyl)-3-(1-piperidyl)-1-ethoxy-2-ethoxycarbonyl-1-propen-1-olato]zinc(II) Bis(trimethylsilyl)amide (5):** A solution of 335 mg of 1-(2-pyridyl)-1-piperidyl-2,2-bis(ethoxycarbonyl)ethane (**4**) (335 mg, 1.0 mmol) in 3 mL of anhydrous toluene was cooled to –78 °C and 386 mg of $Zn[N(SiMe_3)_2]_2$ (1.0 mmol) were added dropwise. After complete addition the solution was warmed to room temp. and the volume reduced to half of the original volume. At –20 °C, 380 mg of colorless prisms of **5** (0.68 mmol, 68%) crystallized and were isolated, washed with a small amount of pentane and dried in vacuo; m.p. 172 °C (dec.). $^1$H NMR ([D$_6$]benzene): $\delta$ = 7.87 [d, $^3J$(H,H) = 5.2 Hz, 1 H, Pyr1], 7.45 [d, $^3J$(H,H) = 7.6 Hz, 1 H, Pyr4], 6.78 [dt, $^3J$(H,H) = 7.6, $^5J$(H,H) = 1.6 Hz, 1 H, Pyr3], 6.25 (m, 1 H, Pyr2), 5.40 (s, 1 H, CHN), 4.44 (m, 2 H, O′$CH_2$), 4.18 (m, 1 H, OCHH$^a$), 4.05 (m, 1 H, OCH$^b$H), 3.70 [d, $^2J(H_{ax},H_{eq})$ = 11.6 Hz, 1 H, Pip2′$_{eq}$], 2.44 [d, $^2J(H_{ax},H_{eq})$ = 11.6 Hz, 1 H, Pip2$_{eq}$], 2.06 [dt, $^2J(H_{ax},H_{eq}) \approx {}^3J(H_{ax},H_{ax})$ = 11.6, $^3J$(H,H) = 2.4 Hz, 1 H, Pip2′$_{ax}$], 1.71 (m, 1 H, Pip3′$_{ax}$), 1.64 (m, 2 H, Pip2$_{ax}$/3$_{ax}$), 1.38 (m, 2 H, Pip3′$_{eq}$/4$_{eq}$), 1.30 [t, $^3J$(H,H) = 7.2 Hz, 3 H, ′$CH_3$], 1.16 (m, 1 H, Pip3$_{eq}$), 1.10 [t, $^3J$(H,H) = 7.2 Hz, 3 H, $CH_3$], 0.84 (m, 1 H, Pip4$_{ax}$), 0.41 [s, 18 H, $Si(CH_3)_3$] ppm. $^{13}$C{$^1$H} NMR ([D$_6$]benzene): $\delta$ = 170.1 (C=O), 169.8 (′C=O), 161.2 (Pyr5), 145.2 (Pyr1), 139.7 (Pyr3), 123.8 (Pyr4), 122.5 (Pyr2), 74.6 [$C(COOEt)_2$], 70.6 (CHN), 61.0 ($OCH_2$), 59.0 (O′$CH_2$), 55.6 (Pip2), 51.3 (Pip2′), 25.4 (Pip3′), 25.0 (Pip3), 23.8 (Pip4), 15.2 (′$CH_3$), 14.9 ($CH_3$), 6.1 [$Si(CH_3)_3$] ppm. IR (Nujol, $cm^{-1}$): $\tilde{\nu}$ = 3067 (w), 2925 (vs), 2854 (vs), 1620 (vs), 1605 (s), 1567 (m), 1521 (vs), 1454 (s), 1415 (s), 1383 (s), 1337 (s), 1300 (m), 1253 (s), 1208 (m), 1169 (s), 1148 (m), 1113 (s), 1099 (s), 1059 (m), 1027 (m), 983 (vs), 883 (s), 833 (s), 791 (m), 751 (w), 670 (m), 613 (w) $cm^{-1}$. MS (DEI): *m/z* (%) = 558 (20) $[M(^{64}Zn)H]^+$, 542 (38) $[M(^{64}Zn) - CH_3]^+$, 473 (100) $[M(^{64}Zn) - C_5H_{10}N]^+$, 349 (87) $[MH - {}^{64}ZnN(Si_2(CH_3)_5]^+$, 204 (91) $[C_{11}H_{10}NO_3]^+$, 146 (98) $[HNSi_2(CH_3)_5]^+$, 130 (95) $[NSi_2(CH_3)_4]^+$, 73 (22) $[Si(CH_3)_3]^+$. $C_{24}H_{43}N_3O_4Si_2Zn$ (559.20): calcd. C 51.55, H 7.75, N 7.51; found C 50.56, H 7.44, N 7.39.

**Bis(trimethylsilyl)methylzinc(II) 1-Ethoxy-2-(ethoxycarbonyl)-3-(1-piperidyl)-3-(2-pyridyl)-1-propen-1-olate (6):** A solution of 335 mg of 2,2-bis(ethoxycarbonyl)-1-(1-piperidyl)-1-(2-pyridyl)ethane (1.0 mmol) in 2 mL of toluene was cooled to –78 °C. A 1.0 M solution of [bis{bis(trimethylsilyl)methyl}zinc] (1.0 mL, 1.0 mmol) in toluene was added dropwise. Thereafter the reaction mixture was warmed to room temp. and then the volume was reduced to approx. 30%. From this clear solution, 490 mg of colorless prisms of **6** (0.88 mmol, 88%) crystallized at –20 °C and were washed with pentane and dried under vacuum; m.p. 185 °C (dec.). $^1$H NMR ([D$_6$]-benzene): $\delta$ = 8.04 [d, $^3J$(H,H) = 5.2 Hz, 1 H, Pyr1], 7.50 [d, $^3J$(H,H) = 7.6 Hz, 1 H, Pyr4], 6.83 [dt, $^3J$(H,H) = 7.6, $^4J$(H,H) = 1.6 Hz, 1 H, Pyr3], 6.30 (m, 1 H, Pyr2), 5.44 (s, 1 H, CHN), 4.45 (m, 2 H, O′$CH_2$), 4.17 (m, 1 H, OCH$_a$H), $\delta$ = 4.05 (m, 1 H, OCHH$_b$), 3.31 [d, $^2J(H_{ax},H_{eq})$ = 11.6 Hz, 1 H, Pip2′$_{eq}$], 2.41 [d, $^2J(H_{ax},H_{eq})$ = 11.6 Hz, 1 H, Pip2$_{eq}$], 2.13 (m, 1 H, Pip2′$_{ax}$), 1.64 (m, 1 H, Pip2$_{ax}$), 1.59–1.38 (m, 3 H, Pip3$_a$/3′$_{a/b}$), 1.30 [t, $^3J$(H,H) = 7.2 Hz, 4 H, O′$CH_2C\mathit{H}_3$, Pip4$_a$], 1.17 (m, 1 H, Pip3$_b$), 1.13 [t, $^3J$(H,H) = 7.2 Hz, 3 H, $OCH_2C\mathit{H}_3$], 0.87 (m, 1 H, Pip4$_b$), 0.42 [s, 9 H, ′$Si(CH_3)_3$], 0.31 [s, 9 H, $Si(CH_3)_3$], –0.84 [s, 1 H, C*H*(Si-$(CH_3)_3)_2$] ppm. $^{13}$C{$^1$H} NMR ([D$_6$]benzene): $\delta$ = 170.0 (C=O), 169.8 (′C=O), 162.0 (Pyr5), 145.1 (Pyr1), 139.5 (Pyr3), 123.9 (Pyr4), 122.4 (Pyr2), 74.5 [*C*$(COOEt)_2$], 70.4 (CHN), 59.8 ($OCH_2$), 58.9 (O′$CH_2$), 55.1 (Pip2), 50.9 (Pip2′), 25.0 (Pip3′), 24.3 (Pip3), 23.9 (Pip4), 15.2 (′$OCH_2C\mathit{H}_3$), 14.9 ($OCH_2C\mathit{H}_3$), 4.9 [$Si(CH_3)_3$], 4.3 [′$Si(CH_3)_3$], 0.5 {*C*H$Si[(CH_3)_3]_2$} ppm. IR (Nujol): $\tilde{\nu}$ = 3067 (w), 2925 (vs), 2854 (vs), 1620 (vs), 1605 (s), 1565 (m), 1519 (vs), 1471 (s), 1414 (s), 1383 (s), 1337 (s), 1300 (m), 1267 (m), 1244 (s), 1209 (m), 1169 (s), 1150 (m), 1114 (s), 1101 (m), 1070 (m), 1060 (m), 1029 (m), 960 (m), 897 (s), 868 (s), 850 (vs), 781 (m), 745 (w), 670 (m), 647 (w), 615 (w), 492 (w), 496 (w) $cm^{-1}$. MS (DEI): *m/z* (%) = 556 (20) $[M(^{64}Zn)]^+$, 541 (16) $[M(^{64}Zn) - CH_3]^+$, 472 (77) $[M(^{64}Zn) - C_5H_{10}N]^+$, 204 (97) $[C_{11}H_{10}NO_3]^+$, 174 (100), 129 (46) $[HCSi_2(CH_3)_4]^+$, 84 (15) $[C_5H_{10}N]^+$, 73 (11) $[Si(CH_3)_3]^+$. $C_{25}H_{44}N_2O_4Si_2Zn$ (558.19): calcd. C 53.79, H 7.95, N 5.02; found C 53.67, H 8.05, N 5.06.

**1-Ethoxy-2-(ethoxycarbonyl)-1-lithoxy-3-(1-piperidyl)-3-(2-pyridyl)-1-propene (7):** A solution of 240 mg of 2,2-bis(ethoxycarbonyl)-1-(1-piperidyl)-1-(2-pyridyl)ethane (0.72 mmol) in 2 mL of toluene was cooled to –78 °C. A solution of 120 mg of $LiN(SiMe_3)_2$ in 2 mL of toluene was added dropwise. Thereafter the reaction mixture was warmed to room temp. and the volume reduced to 1 mL. Then 3 mL of pentane were added and all solids removed by filtration. At 20 °C, 210 mg of colorless needles of **7** (0.62 mmol; 85.7%) precipitated and were dried under reduced pressure; m.p. 160 °C (dec.). $^1$H NMR ([D$_6$]benzene): $\delta$ = 8.64 (m, 1 H, Pyr1), 7.30 (m, 1 H, Pyr4), 6.96 (m, 1 H, Pyr3), 6.61 (m, 1 H, Pyr2), 5.35 (m, 1 H, CHN), 4.42–3.59 (m, 4 H, $OCH_2$), 3.67 (m, 1 H, Pip2′$_{eq}$), 3.26 (m, 1 H, Pip2$_{eq}$), 2.37–0.76 (m, 14 H, Pip2$_{ax}$/2′$_{ax}$, Pip3/3′/4, $CH_3$) ppm. $^{13}$C{$^1$H} NMR ([D$_6$]benzene): $\delta$ = 171.8–169.7 (C=O), 167.0 (Pyr5), 147.0 (Pyr1), 136.2 (Pyr3), 123.7 (Pyr4), 120.2 (Pyr2), 76.3 [*C*$(COOEt)_2$], 68.8 (CHN), 58.0–56.9 ($OCH_2$), 56.3 (Pip2), 51.2 (Pip2′), 26.1 (Pip3/3′/4), 15.7–14.9 ($CH_3$) ppm. $^7$Li{$^1$H} NMR ([D$_6$]benzene): $\delta$ = 2.07 ppm. IR (Nujol): $\tilde{\nu}$ = 2924 (vs), 2854 (vs), 2809 (m), 1673 (vs), 1596 (m), 1570 (m), 1524 (s), 1464 (s), 1407 (s), 1377 (s), 1350 (m), 1294 (s), 1259 (s), 1214 (m), 1164 (m), 1093 (s), 1064 (vs), 1007 (m), 977 (s), 854 (m), 791 (m), 751 (m), 729 (w), 686 (w), 637 (w) $cm^{-1}$. MS (FAB): *m/z* (%) = 505 (23) $[M + C_7H_{10}O_4Li]^+$, 347 (8) $[M + Li]^+$, 335 (9) $[M + 2H^+ - Li]^+$, 256 (55) $[M - C_5H_{10}N]^+$, 250 (50) $[M + H - LiC_5H_{10}N]^+$, 204 (100)

$[C_{11}H_{10}NO_3]^+$. $C_{18}H_{25}LiN_2O_4$ (340.34): calcd. C 63.52, H 7.40, N 8.23; found C 62.04, H 7.14, N 7.77.

**Sodium 1-Ethoxy-2-(ethoxycarbonyl)-3-(1-piperidyl)-3-(2-pyridyl)-1-propen-1-olate (8):** A solution of 502 mg of 2,2-bis(ethoxycarbonyl)-1-(1-piperidyl)-1-(2-pyridyl)ethane (1.5 mmol) in 3 mL of 1,2-dimethoxyethane (DME) was dropped to a suspension of 36 mg of NaH (1.5 mmol) in 2 mL of DME. This mixture was stirred at room temp. till no gas evolution was observed (approximately 12 h). The precipitating slightly orange solid (500 mg, 1.4 mmol, 94%) was collected, washed with DME and dried in vacuo; m.p. 205 °C (dec.). $^1$H NMR ([D$_6$]DMSO): $\delta$ = 8.24 [d, $^3J$(H,H) = 4.4 Hz, 1 H, Pyr1], 7.51 (m, 2 H, Pyr3/4), 6.94 [dd, $^3J$(H,H) = 8.8, $^3J$(H,H) = 4.4 Hz, 1 H, Pyr2], 4.82 (s, 1 H, CHN), 3.72 (m, 4 H, $OCH_2$), 2.50 (m, 2 H, Pip2), 2.29 (m, 2 H, Pip2′), 1.50 (m, 4 H, Pip3/3′), 1.34 (m, 2 H, Pip4), 0.92 (m, 6 H, $CH_3$) ppm. $^{13}$C{$^1$H} NMR ([D$_6$]DMSO): $\delta$ = 169.3 (C=O), 167.4 (Pyr5), 146.9 (Pyr1), 134.3 (Pyr3), 122.3 (Pyr4), 119.1 (Pyr2), 73.8 [*C*(COOEt)$_2$], 68.7 (CHN), 55.6 ($OCH_2$), 51.9 (Pip2/2′), 26.2 (Pip3/3′), 24.8 (Pip4), 14.9 ($CH_3$) ppm. IR (Nujol, cm$^{-1}$): $\tilde{\nu}$ = 2924 (vs), 2854 (vs), 2809 (m), 1677 (vs), 1595 (m), 1566 (m), 1527 (s), 1463 (s), 1401 (m), 1378 (s), 1337 (m), 1288 (s), 1248 (m), 1212 (m), 1155 (m), 1108 (m), 1067 (s), 1055 (vs), 1004 (w), 983 (s), 852 (m), 788 (m), 756 (m), 731 (w), 684 (w), 633 (w) cm$^{-1}$. MS (Micro-ESI pos. in ethanol): *m*/*z* (%) = 357 ([MH]$^+$, 18), 335 ([MH$_2$]$^+$ – Na$^+$, 100), 250 ([MH – NaC$_5$H$_{10}$N]$^+$, 38). $C_{18}H_{25}N_2NaO_4$ (356.40): calcd. C 60.66, H 7.07, N 7.86; found C 58.84, H 7.18, N 7.51.

**Synthesis of *N*-(2-Pyridylmethyl)benzoylamine (9):** Benzoyl chloride (3.83 g, 27.3 mmol) was added at 0 °C to a solution of 6.06 g of (2-pyridylmethyl)(*tert*-butyldimethylsilyl)amine (27.3 mmol) in 25 mL of toluene. The solution turned yellow and a colorless precipitate formed. All solids were removed and cooling of the filtrate to –20 °C yielded 5.34 g of yellow crystalline **8** (25.2 mmol, 92%); m.p. 66 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 8.48 [d, $^3J$(H1,H2) = 4.8 Hz, 1 H, Pyr1], 7.83 [d, $^3J$(H9,H10) = 5.2 Hz, 1 H, Ph9], 7.78 (s, 1 H, NH), 7.61 [dt, $^5J$(H3,H1) = 1.6, $^3J$(H3,H2/4) = 6 Hz, 1 H, Pyr3], 7.44 [t, $^3J$(H11,H10) = 3.6 Hz, 1 H, Ph11], 7.36 [t, $^3J$(H10,H9/11) = 6.4 Hz, 1 H, Ph10], 7.26 [d, $^3J$(H4,H3) = 7.6 Hz, 1 H, Pyr4], 7.14 [t, $^3J$(H1,H3) = 9.2 Hz, 1 H, Pyr2], 4.69 [d, $^3J$(H6,NH) = 4.8 Hz, 2 H, $CH_2$] ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 167.3 (C=O), 156.3 (Pyr5), 148.8 (Pyr1), 136.7 (Pyr3), 134.2 (Ph8), 131.3 (Ph11), 128.4 (Ph10), 127.0 (Ph9), 122.3 (Pyr2), 122.0 (Pyr4), 44.7 ($^2J$, $CH_2$) ppm. IR (Nujol, cm$^{-1}$): $\tilde{\nu}$ = 3288 (vs), 2923 (vs), 2854 (vs), 2550 (s), 2058 (w), 1981 (w), 1646 (vs), 1580 (m), 1539 (vs), 1490 (s), 1466 (s), 1397 (m), 1328 (m), 1311 (s), 1283 (s), 1249 (w), 1171 (w), 1077 (w), 1036 (m), 1001 (w), 961 (w), 931 (vw), 839 (w), 772 (s), 714 (s), 691 (m), 627 (m), 594 (w), 506 (vw) cm$^{-1}$. MS (DEI): *m*/*z* (%) = 212 (76) [M$^+$], 135 (14) [M$^+$ – C$_6$H$_5$], 107 (91) [C$_6$H$_7$N$_2$]$^+$, 92 (34) [C$_6$H$_6$N]$^+$, 77 (100) [C$_6$H$_5^+$]. $C_{13}H_{12}N_2O$ (212.25): calcd. C 73.57, H 5.70, N 13.20; found C 72.64, H 5.55, N 13.39.

**Synthesis of *N*-(2-Pyridylmethyl)dibenzoylamine (10):** A solution of 141 mg of *N*-(2-pyridylmethyl)benzoylamin (**9**) (0.66 mmol) in 5 mL of toluene was cooled to 0 °C. Then 1.2 mL of a 1.6 M butyllithium solution in hexane was added dropwise. This red reaction mixture was stirred for 10 min and thereafter, 0.31 g of benzoyl chloride was added slowly. The color of the solution turned green and LiCl precipitated. After filtration, a separation via column chromatography gave 40 mg of green oily **10** (0.13 mmol, 19%). $^1$H NMR ($CDCl_3$): $\delta$ = 8.53 (d, 1 H, Pyr1), 8.08 (d, 1 H, Ph9), 7.66 [dt, $^5J$(H3,H1) = 2.0, $^3J$(H3,H2/4) = 7.8 Hz, 1 H, Pyr3], 7.60 (m, 4 H, Ph11/Ph10), 7,47–7.36 (m, 3 H, Ph10/Pyr4), 7,26–7.11 (m, 4 H, Ph11/Ph9/Pyr2), 5.36 (s, 2 H, $CH_2$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 173.9 (C=O), 170.8 (C=O), 156.2 (Pyr5), 148.9 (Pyr1), 136.4 (Pyr3), 136.1 (Ph8), 133.2 (Ph11), 131.4 (Ph11), 129.8 (Ph10), 129.2 (Ph10), 128.1 (Ph9), 127.8 (Ph9), 121.9 (Pyr2), 121.5 (Pyr4), 51.1 ($^2J$, $CH_2$) ppm. IR (Nujol): $\tilde{\nu}$ = 2923 (vs), 2854 (vs), 1722 (w), 1656 (vs), 1582 (m), 1489 (m), 1468 (m), 1409 (m), 1332 (s), 1287 (s), 1237 (s), 1173 (m), 1136 (m), 1041 (m), 1017 (s), 996 (s), 803 (w), 775 (m), 714 (s), 508 (vw) cm$^{-1}$. MS (DEI): *m*/*z* (%) = 315 (6) [M – 1], 211 (28) [M C$_7$H$_5$O], 107 (93) [C$_6$H$_7$N$_2$]$^+$, 92 (22) [C$_6$H$_6$N]$^+$, 77 (100) [C$_6$H$_5$].

**Synthesis of (Diphenylmethylidene)(2-pyridylmethyl)amine (11):** A mixture of 3.97 g of (2-pyridylmethyl)amine (0.037 mol), 6.69 g of benzophenone (0.037 mol) and 10 mg of *p*-toluenesulfonic acid in 50 mL of anhydrous toluene was stirred for 14 hours under reflux. During the reaction the color changed from light to dark yellow. At the end of the reaction the mixture was cooled to room temp. Then it was washed with 10 mL of a 10% aqueous sodium carbonate solution, three times with 10 mL of 2% aqueous sodium hydroxide solution and then three times with 10 mL of water. The organic layer was separated and dried with sodium sulfate. After removal of the drying agent most of the toluene was removed in vacuo. Bulb-to-bulb distillation at 150 °C and $8 \times 10^{-3}$ mbar afforded 6.0 g of a yellow oil (yield 49%). However, **11** still contained traces of benzophenone. The substance can be used for complexation reactions without further purification or transferred into its hydrochloride. For this purpose, 6.8 g of impure **11** was dissolved in 50 mL of anhydrous diethyl ether at 0 °C. Now 3 mL of a solution of 4.7% HCl in anhydrous diethyl ether were added slowly and under vigorous stirring in an argon atmosphere yielding a white hygroscopic precipitate. The precipitate **11**·HCl was isolated, washed three times with anhydrous diethyl ether and dried in vacuo. Overall yield 46%. $^1$H NMR ($CD_2Cl_2$): $\delta$ = 4.78 (s, 2 H, $CH_2$), 7.81 (ddd, *J* = 1.6, *J* = 6.4 Hz, 1 H, Pyr5), 7.94 (t, *J* = 7.6 Hz, 4 H, Ph15), 8.01 (d, *J* = 8.0 Hz, 1 H, Pyr3), 8.06 (ddd, *J* = 1.2, *J* = 6.4 Hz, 2 H, Ph16), 8.17 (d, *J* = 8.4 Hz, 4 H, Ph14), 8.30 (ddd, *J* = Pyr4, 1.6 Hz, 1 H, 7.6 Hz), 9.01 (d, *J* = 4.8 Hz, 1 H, Pyr6) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$): $\delta$ = 44.1 ($CH_2$), 124.1 (Pyr3), 124.6 (Pyr5), 129.2 (Ph15, Ph), 130.6 (Ph14), 133.4 (Ph16), 138. 5 (Ph13), 138.8 (Pyr4), 150.0 (Pyr6), 153.4 (Pyr2), 196.7 (C=N) ppm. IR (Nujol): $\tilde{\nu}$ = 2616 (st, N–H–N), 2404 (st, N–H–N), 2085 (w), 1989 (w), 1666 (w), 1630 (st), 1597 (m), 1348 (m), 1313 (m), 1277 (m), 1150 (w), 1025 (w), 940 (w), 777 (st), 701 (st), 639 (w), 610 (w), 565 (w) cm$^{-1}$. MS (ESI): *m*/*z* (%) = 273 (100) [M – Cl]$^+$, 198 (20), 167 (1), 109 (2).

**[(Diphenylmethylidene)(2-pyridylmethyl)amino]zinc(II) Chloride (12):** A solution of 1.36 g of (diphenylmethylidene)(2-pyridylmethyl)amine (5 mmol) in 5 mL of THF was dropped at room temp. into a solution of 0.68 g of anhydrous zinc dichloride (5 mmol) in 5 mL of THF. Stirring at room temperature for one hour yielded 1.22 g of a colorless crystalline precipitate of **12** (3.0 mmol, 60%) which was collected and recrystallized from THF solution at –20 °C. $^1$H NMR ($CH_2Cl_2$): $\delta$ = 5.00 (s, 2 H, $CH_2$), 7.30–7.32 (m, 2 H, Ph14), 7.34 (d, *J* = 8.0 Hz, 1 H, Pyr3), 7.50 (t, *J* = 8.0 Hz, 2 H, Ph15a), 7.54–7.62 (m, 5 H, Pyr5, Ph15, Ph16, Ph16a), 7.80 (d, *J* = 8.0 Hz, 2 H, Ph14a), 7.98 (ddd, *J* = 1.2, *J* = 8.0 Hz, 1 H, Pyr4), 8.65 (d, *J* = 8.0 Hz, 1 H, Pyr6) ppm. $^{13}$C{$^1$H} NMR ($CH_2Cl_2$): $\delta$ = 56.5 ($CH_2$), 123.2 (Pyr3), 125.2 (Pyr5), 127.6 (Ph14), 129.2 (Ph15a), 129.8 (Ph15), 130.0 (Ph14a), 131.1 (Ph16), 133.1 (Ph16a), 135.8 (Ph13), 138.5 (Ph13a), 141.1 (Pyr4), 148.1 (Pyr6), 155.2 (Pyr2), 181.6 (C=N) ppm. MS (DEI): *m*/*z* (%) = 373 (19) [M – Cl]$^+$, 272 180 (100) (98), 193 (50), 165 (42), 91 (51), 77 (30), 65 (25), 51 (19). IR (Nujol): $\tilde{\nu}$ = 3091 (w), 3061 (w), 1622 (st, C=N), 1606 (st), 1573 (m), 1486 (st), 1442 (st), 1411 (st), 1361 (m), 1325 (m), 1301 (m), 1282 (m), 1232 (w), 1214 (w), 1156 (m), 1079 (w), 1046 (st), 1030 (st), 999 (w), 972 (w), 927 (w), 844 (w), 785

Table 4. Crystal data and refinement details for the X-ray structure determinations of the isotypic compounds **1** to **5** as well as **5**·1/2 toluene and **6**.

| Compound | **1** | **4** | **5** | **6** | **7** | **9** | **12** | **14** |
|---|---|---|---|---|---|---|---|---|
| Formula | $C_{50}H_{62}Li_2N_4O_2Si_2$ | $C_{18}H_{26}N_2O_4$ | $C_{24}H_{43}N_3O_4Si_2Zn$ | $C_{25}H_{44}N_2O_4Si_2Zn$ | $C_{72}H_{100}Li_4N_8O_{16}$ | $C_{13}H_{12}N_2O$ | $C_{19}H_{16}Cl_2N_2Zn$ | $[C_{26}H_{21}N_2O]^+$ $[C_4H_8Cl_3OZn]^-$ |
| $Fw$ (g mol$^{-1}$) | 821.10 | 334.41 | 559.16 | 558.17 | 1361.36 | 212.25 | 408.61 | 621.27 |
| $T$/°C | –90(2) | –90(2) | –90(2) | –90(2) | –90(2) | –90(2) | –90(2) | –90(2) |
| Crystal system | triclinic | orthorhombic | triclinic | triclinic | triclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ | $Pca2_1$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 9.3163(10) | 8.7613(3) | 8.6564(3) | 8.7050(3) | 14.6163(5) | 11.1667(5) | 10.0416(4) | 16.7901(5) |
| $b$/Å | 11.1849(13) | 23.9270(6) | 9.6259(3) | 9.6937(3) | 15.7628(6) | 20.6651(9) | 11.3596(4) | 9.0266(4) |
| $c$/Å | 12.6410(16) | 17.4661(7) | 19.6991(9) | 19.9190(7) | 20.3099(8) | 9.6913(3) | 16.1273(5) | 19.3853(9) |
| $\alpha$/° | 112.229(7) | 90.00 | 101.171(3) | 101.234(2) | 83.186(2) | 90.00 | 90.00 | 90.00 |
| $\beta$/° | 102.238(6) | 90.00 | 93.557(3) | 93.247(2) | 86.557(2) | 90.258(2) | 99.615(2) | 104.958(3) |
| $\gamma$/° | 90.334(6) | 90.00 | 112.797(2) | 113.217(2) | 85.903(2) | 90.00 | 90.00 | 90.00 |
| $V$/Å$^3$ | 1186.2(2) | 3661.4(2) | 1467.39(10) | 1498.43(9) | 4628.1(3) | 2236.35(16) | 1813.78(11) | 2838.4(2) |
| $Z$ | 1 | 8 | 2 | 2 | 2 | 8 | 4 | 4 |
| $\rho$/g cm$^{-3}$ | 1.149 | 1.213 | 1.266 | 1.237 | 0.977 | 1.261 | 1.496 | 1.454 |
| $\mu$/cm$^{-1}$ | 1.16 | 0.86 | 9.5 | 9.3 | 0.68 | 0.82 | 16.5 | 11.78 |
| Measured data | 8007 | 21481 | 9809 | 11062 | 31386 | 14861 | 12005 | 18748 |
| Data with $I > 2\sigma(I)$ | 2864 | 6051 | 5031 | 5252 | 10613 | 3423 | 3090 | 3638 |
| Unique data/$R_{int}$ | 5215/0.0572 | 7936/0.0682 | 6448/0.0381 | 6789/0.0304 | 20216/0.0379 | 5094/0.0512 | 4127/0.0468 | 6464/0.0874 |
| $wR_2$ (all data, on $F^2$)[a] | 0.2238 | 0.1504 | 0.1155 | 0.0950 | 0.2936 | 0.1440 | 0.0810 | 0.1091 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0769 | 0.0574 | 0.0447 | 0.0391 | 0.0923 | 0.0553 | 0.0338 | 0.0460 |
| $s$[b] | 1.039 | 1.027 | 1.043 | 1.013 | 1.039 | 1.031 | 0.982 | 0.944 |
| Resid. electron dens./e Å$^{-3}$ | 0.343/–0.407 | 0.293/–0.203 | 0.471/–0.527 | 0.291/–0.412 | 0.484/–0.348 | 0.178/–0.194 | 0.335/–0.409 | 0.368/–0.438 |
| Abs. method | multi-scan | multi-scan | multi-scan | multi-scan | multi-scan | multi-scan | multi-scan | multi-scan |
| Abs. corr., transm.$_{min/max}$ | 0.9610/1.0249 | 0.9549/0.9856 | 0.8717/0.9243 | 0.7924/0.9430 | 0.9638/1.0101 | 0.9632/0.9991 | 0.7775/0.8505 | 0.8549/0.8856 |
| CCDC number[46] | 664403 | 664404 | 664405 | 664406 | 664407 | 664408 | 664409 | 664410 |

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

(m), 776 (m), 760 (st), 740 (w), 721 (m), 711 (st), 702 (st), 663 (w), 650 (w), 633 (w), 581 (w), 472 (w) cm$^{-1}$. $C_{19}H_{16}Cl_2N_2Zn$ (408.658): calcd. C 55.84, H 3.95, N 6.85, Cl 17.35; found C 54.55, H 3.77, N 6.54, Cl 17.88.

***N*-(Diphenylchloromethyl)-*N*-(2-pyridylmethyl)benzoylamine (13):** A solution of 0.92 g of (diphenylmethylidene)(2-pyridylmethyl)amine (3.4 mmol) in 10 mL of toluene was cooled to 0 °C. Then 0.4 mL of benzoyl chloride (3.4 mmol) was added slowly. The yellow precipitate of **13** (0.81 g, 1. 96 mmol, 58%) was collected and dried in vacuo. $^1$H NMR ($CDCl_3$): $\delta$ = 8.98 [d, $^3J$(H1,H2) = 8.0 Hz, 1 H, Pyr1], 8.75 [t, $^3J$(H2,H4) = 7.6 Hz, 1 H, Pyr3], 8.36 [d, $^3J$(H4,H3) = 6.0 Hz, 1 H, Pyr4], 8.21 [t, $^3J$(H1,H3) = 6.6 Hz, 1 H, Pyr2], 8.00–7.14 (m, 15 H, Ph), 5.91 (s, 2 H, $CH_2$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 168.0 (C=O), 151.8 (Pyr5), 147.7 (Pyr3), 138.0 (Pyr1), 127.1 (Pyr 2), 132,8–126.5 (Ph), 126.0 (Pyr4), 97.4 [$C(Ph)_2$], 53.5 ($CH_2$) ppm. IR (Nujol): $\tilde{\nu}$ = 2924 (vs), 2854 (vs), 1783 (vw), 1741 (vw), 1662 (s), 1626 (m), 1599 (m), 1578 (w), 1495 (m), 1448 (s), 1378 (vs), 1318 (w), 1278 (m), 1216 (m), 1174 (w), 1137 (w), 1099 (w), 999 (w), 921 (vw), 850 (vw), 750 (m), 700 (s), 672 (w), 638 (w), 629 (w), 616 (vw) cm$^{-1}$. MS (DEI): $m/z$ (%) = 377 (42) [M – Cl], 272 (34) [$M^+$ – $C_7H_5OCl$], 180 (28) $[C_{13}H_{10}N]^+$, 166 (22) $[C_{13}H_{10}]^+$, 105 (76) $[C_6H_5O]^+$, 78 (10) [$C_6H_5$ + $H^+$].

**Zincate 14:** A solution of 0.1 g of $ZnCl_2$ (0.75 mmol) in 5 mL of THF was dropped into a solution of 0.31 g of **13** in 10 mL of THF and 1 mL of chloroform. Cooling of this yellow reaction mixture to –20 °C afforded 0.38 g of colorless crystals of **14** (0.61 mmol, 82%), m.p. 157 °C. $^1$H NMR ($CDCl_3$): $\delta$ = 8.66 [d, $^3J$(H1,H2) = 6.4 Hz, 1 H, Pyr1], 8.57 [t, $^3J$(H2,H4) = 7.2 Hz, 1 H, Pyr3], 8.18 [d, $^3J$(H4,H3) = 8.0 Hz, 1 H, Pyr4], 7.94 [t, $^3J$(H1,H3) = 7.2 Hz, 1 H, Pyr2], 7.30–7.48 (m, 15 H, Ph), 5.58 (s, 2 H, $CH_2$) ppm. $^{13}$C{$^1$H}NMR ($CDCl_3$): $\delta$ = 168.0 (C=O), 150,5 (Pyr5), 147.0 (Pyr3), 138.3 (Pyr1), 127.2 (Pyr 2), 123.6 (Pyr4), 134,3–125,8; 96.8 [$C(Ph)_2$], 67.0 (THF), 52.3 ($CH_2$), 24.6 (THF) ppm. IR (Nujol, cm$^{-1}$): $\tilde{\nu}$ = 3087 (w), 2924 (vs), 2854 (vs), 1663 (vs), 1629 (m), 1579 (w), 1499 (s), 1453 (s), 1378 (vs), 1293 (vw), 1224 (w), 1137 (w), 1099 (w), 1031 (vw), 1001 (vw), 969 (vw), 921 (vw), 854 (w), 777 (m), 748 (s), 725 (s), 716 (s), 701 (s), 672 (w), 638 (m), 606 (vw) cm$^{-1}$. MS (DEI): $m/z$ (%) = 377 (14) [$C_{26}H_{21}N_2O$], 272 (92) $[C_{19}H_{16}N_2]^+$, 180 (90) $[C_{13}H_{10}N]^+$, 166 (54) $[C_{13}H_{10}]^+$, 105 (100) $[C_6H_5O]^+$, 77 (10) [$C_6H_5$], 72 (54) [THF], 39 (62) [$Cl^-$], 37 (46) [$Cl^-$].

**X-ray Structure Determination of 1, 4, 5, 6, 7, 9, 12 and 14:**[46] Intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation. Data were corrected for Lorentz polarization and for absorption effects.[47–49] Crystallographic data as well as structure solution and refinement details are summarized in Table 4.

The structures were solved by direct methods (SHELXS[50]) and refined by full-matrix least-squares techniques against $F_o^2$ (SHELXL-97[51]). For the amino groups of **1** and **9**, for the whole compound **12** and for the methine group C19 of **6** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically.[51] The quality of structure determination of **7** is rather poor due to thermal motion and disordering as a consequence of the large gaps between the tetramers. XP (SIEMENS Analytical X-ray Instruments, Inc.) and POVRAY were used for structure representations.

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[1] H.-B. Kraatz, N. Metzler-Nolte, *Concepts and Models in Bioinorganic Chemistry*, Wiley-VCH, Weinheim, **2006**.
[2] G. Parkin, *Chem. Rev.* **2004**, *104*, 699–767.
[3] a) G. J. Sutton, *Aust. J. Chem.* **1961**, *14*, 545; b) G. J. Sutton, *Aust. J. Chem.* **1963**, *16*, 1137–1140.
[4] M. Noji, Y. Kidani, H. Koike, *Bull. Chem. Soc. Jpn.* **1975**, *48*, 245–249.
[5] a) M. L. Niven, G. C. Percy, *Spec. Lett.* **1977**, *10*, 519–525; b) M. L. Niven, G. C. Percy, *J. Mol. Struct.* **1980**, *68*, 73–80.
[6] M. Mikami-Kido, Y. Saito, *Acta Crystallogr., Sect. B* **1982**, *38*, 452–455.
[7] C. Engelter, G. E. Jackson, C. L. Knight, D. A. Thornton, *J. Coord. Chem.* **1989**, *20*, 297–306.
[8] D. J. Hodgson, K. Michelsen, E. Pedersen, *Acta Chem. Scand.* **1990**, *44*, 1002–1005.
[9] M. Westerhausen, T. Bollwein, K. Polborn, *Z. Naturforsch., Teil B* **2000**, *55*, 51–59.
[10] M. Westerhausen, T. Bollwein, P. Mayer, H. Piotrowski, A. Pfitzner, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1425–1432.
[11] M. Westerhausen, T. Bollwein, N. Makropoulos, T. M. Rotter, T. Habereder, M. Suter, H. Nöth, *Eur. J. Inorg. Chem.* **2001**, 851–857.
[12] M. Westerhausen, T. Bollwein, N. Makropoulos, S. Schneiderbauer, M. Suter, H. Nöth, P. Mayer, H. Piotrowski, K. Polborn, A. Pfitzner, *Eur. J. Inorg. Chem.* **2002**, 389–404.
[13] D. Olbert, A. Kalisch, N. Herzer, H. Görls, P. Mayer, L. Yu, M. Reiher, M. Westerhausen, *Z. Anorg. Allg. Chem.* **2007**, *633*, 893–902.
[14] J. T. B. H. Jastrzebski, J. M. Klerks, G. van Koten, K. Vrieze, *J. Organomet. Chem.* **1981**, *210*, C49–C53.
[15] G. van Koten, J. T. B. H. Jastrzebski, K. Vrieze, *J. Organomet. Chem.* **1983**, *250*, 49–61.
[16] A. L. Spek, J. T. B. H. Jastrzebski, G. van Koten, *Acta Crystallogr., Sect. C* **1987**, *43*, 2006–2007.
[17] E. Wissing, S. van der Linden, E. Rijnberg, J. Boersma, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1994**, *13*, 2602–2608.
[18] M. Westerhausen, T. Bollwein, K. Karaghiosoff, S. Schneiderbauer, M. Vogt, H. Nöth, *Organometallics* **2002**, *21*, 906–911.
[19] B. Baruah, D. Prajapati, J. S. Sandhu, *Tetrahedron Lett.* **1995**, *36*, 6747–6750.
[20] a) A. Alexakis, I. Aujard, P. Mangeney, *SYNLETT* **1998**, 873–874; b) A. Alexakis, I. Aujard, P. Mangeney, *SYNLETT* **1998**, 875–876.
[21] M. Westerhausen, A. N. Kneifel, N. Makropoulos, *Inorg. Chem. Commun.* **2004**, *7*, 990–993.
[22] A. N. Kneifel, Dissertation, Munich **2005**.
[23] J. M. Sprake, K. D. Watson, *J. Chem. Soc. Perkin Trans. 1* **1976**, 5–8.
[24] B. C. Ranu, R. Jana, *Eur. J. Org. Chem.* **2006**, 3767–3770.
[25] Y. Shen, B. Yang, *J. Organomet. Chem.* **1989**, *375*, 45–49.
[26] Z. Zhou, L. Shi, Y. Huang, *Synth. Commun.* **1991**, *21*, 1027–1037.
[27] S. F. Wnuk, E. Lewandowska, C. A. Valdez, S. Kinastowski, *Tetrahedron* **2000**, *56*, 7667–7671.
[28] S. Kinastowski, S. Wnuk, *Synthesis* **1983**, 654–659.
[29] a) A. Mondal, Y. Li, M. A. Khan, J. H. Ross, R. P. Houser, *Inorg. Chem.* **2004**, *43*, 7075–7082; b) U. P. Chaudhuri, L. R. Whiteaker, L. Yang, R. P. Houser, *Dalton Trans.* **2006**, 1902–1908; c) L. Yang, R. P. Houser, *Inorg. Chem.* **2006**, *45*, 9416–9422.
[30] T. Okuyama, H. Shibuya, T. Fueno, *J. Am. Chem. Soc.* **1982**, *104*, 730–736.
[31] K. Gregory, P. v. R. Schleyer, R. Snaith, *Adv. Inorg. Chem.* **1991**, *37*, 47–142.
[32] F. Pauer, P. P. Power in A.-M. Sapse, P. v. R. Schleyer (eds.): *Lithium Chemistry: A Theoretical and Experimental Overview*; Wiley: New York, **1995**; chap. 9, pp. 295–392.
[33] G. Markgraf, H.-W. Lerner, M. Bolte, M. Wagner, *Z. Anorg. Allg. Chem.* **2004**, *630*, 217–218.
[34] A. Haaland, K. Hedberg, P. P. Power, *Inorg. Chem.* **1984**, *23*, 1972–1975.
[35] S. C. Goel, M. Y. Chiang, W. E. Buhro, *Inorg. Chem.* **1990**, *29*, 4646–4652.
[36] H. Schumann, J. Gottfriedsen, S. Dechert, F. Girgsdies, *Z. Anorg. Allg. Chem.* **2000**, *626*, 747–758.
[37] J. M. Bakker, G. B. Deacon, P. C. Junk, G. J. Moxey, D. R. Turner, *Z. Anorg. Allg. Chem.* **2007**, *633*, 251–255.
[38] M. A. Putzer, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **1997**, *623*, 539–544.
[39] G. C. Forbes, A. R. Kennedy, R. E. Mulvey, B. A. Roberts, R. B. Rowlings, *Organometallics* **2002**, *21*, 5115–5121.
[40] K. F. Tesh, T. P. Hanusa, J. C. Huffman, *Inorg. Chem.* **1990**, *29*, 1584–1586.
[41] G. Becker, K. Hübler, M. Niemeyer, N. Seidler, B. Thinus, *Z. Anorg. Allg. Chem.* **1996**, *622*, 197–211.
[42] P. Guo, J. Liu, Z. Fang, A. Mi, Y. Jiang, *Chin. Chem. Lett.* **1991**, *2*, 201–204.
[43] a) P. J. Bonitatebus, W. H. Armstrong, *Chem. Commun.* **1999**, 55–56; b) A. Dashti, K. Niediek, B. Werner, B. Neumüller, *Z. Anorg. Allg. Chem.* **1997**, *623*, 394–402; c) L. Gelmini, W. H. Armstrong, *J. Chem. Soc. Chem. Commun.* **1989**, 1904–1905; d) K. Folting, J. C. Huffman, R. L. Bansemer, K. G. Caulton, J. L. Martin, P. D. Smith, *Inorg. Chem.* **1984**, *23*, 4589–4592; e) K. Folting, J. C. Huffman, R. L. Bansemer, K. G. Caulton, *Inorg. Chem.* **1984**, *23*, 3289–3292.
[44] See for example: a) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 581–587; b) R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 643–648; c) R. G. Parr, R. G. Pearson, *J. Am. Chem. Soc.* **1983**, *105*, 7512–7516; d) R. G. Pearson, *Inorg. Chem.* **1988**, *27*, 734–740; e) R. G. Pearson, *Coord. Chem. Rev.* **1990**, *100*, 403–425; f) R. G. Pearson, *Acc. Chem. Res.* **1993**, *26*, 250–255.
[45] D. Hampe, W. Günther, H. Görls, E. Anders, *Eur. J. Org. Chem.* **2004**, 4357–4372.
[46] CCDC-664403 (for **1**), -664404 (for **4**), -664405 (for **5**), -664406 (for **6**), -664407 (for **7**), -664408 (for **9**), -664409 (for **12**), and -664410 (for **14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[47] *COLLECT*, Data Collection Software, Nonius B. V., The Netherlands, **1998**.
[48] Z. Otwinowski, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, in *Methods in Enzymology* (Eds.: C. W. Carter, R. M. Sweet), vol. 276, *Macromolecular Crystallography*, Part A, pp. 307–326, Academic Press, San Diego, **1997**.
[49] SORTAV, R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
[50] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
[51] G. M. Sheldrick, *SHELXL-97*, release 97-2, University of Göttingen, Germany, **1997**.

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