DOI: 10.1002/ejic.200801136

Synthesis of Trinuclear, Dinuclear and Mononuclear Carbamato-Zinc Complexes from Tetranuclear Precursors: A Top-Down Synthetic Approach to New Carbamates

Dan Domide,[a] Christiane Neuhäuser,[a] Elisabeth Kaifer,[a] Hubert Wadepohl,[a] and Hans-Jörg Himmel*[a]

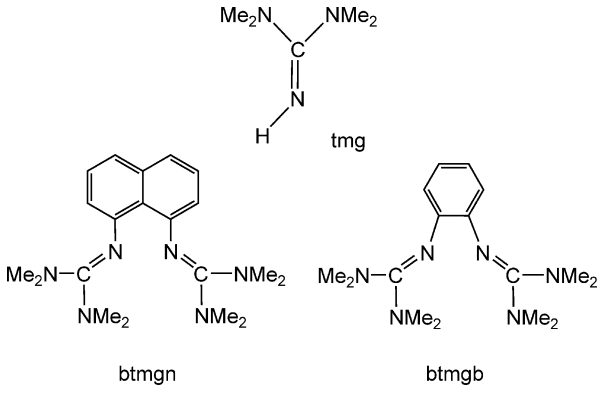
Keywords: Zinc / Oligonuclear complexes / Coordination compounds / Carbamates / Amides / Guanidine

In this work we report on the synthesis of new mono-, bi- and trinuclear carbamato-Zn complexes by reaction of the tetranuclear precursor $[ZnEt(O_2CNR_2)]_4$ (R = *i*Pr and *i*Bu) with the nitrogen bases pyridine, *N*,*N*,*N*′,*N*′-tetramethylguanidine (tmg) and bis(*N*,*N*,*N*′,*N*′-tetramethylguanidino)naphthalene (btmgn). The only reaction product obtained with pyridine is the dinuclear complex $[(py)ZnEt(O_2CNR_2)]_2$. In the case of reaction of $[ZnEt(O_2CNR_2)]_4$ with tmg, the dinuclear species $[(tmg)ZnEt(O_2CNR_2)]_2$ (for molar ratios of 1:4) and the mononuclear bis-carbamato complex $[(tmg)_2Zn(O_2CNR_2)_2]$ (for molar ratios of 1:8) were obtained. Finally, the mono- and trinuclear carbamates $[(btmgn)ZnEt(O_2CNR_2)]$ and $[(btmgn)Zn_3Et_3(O_2CNR_2)_3]$ were formed in the reaction between $[ZnEt(O_2CNR_2)]_4$ and btmgn (molar ratios 1:4 and 1:2, respectively). All products were structurally characterized by X-ray diffraction. Using this top-down approach the synthesis of a variety of oligonuclear carbamato-Zn complexes becomes possible.

Introduction

Several routes leading to zinc carbamates were reported in the literature. For example, tetranuclear carbamato-zinc complexes $[ZnR(O_2CNR'_2)]_4$ are the products of reactions between CO_2 and an alkylzinc amide $[ZnR(NR'_2)]_n$ or a ZnR_2/HNR'_2 mixture (R, R′ = alkyl).[1–3] The possible first steps of this reaction were analysed by quantum chemical calculations.[4] These calculations indicate that the alkylzinc amides react readily without any activation barrier with CO_2 in their monomeric form (n = 1). In contrast, reaction of the dimer $[ZnR(NR'_2)]_2$ is subject to a significant activation barrier. Although numerous examples of carbamato-Zn complexes were synthesized by this route or another, little is known about their reactivity. Highly relevant to this work, $[ZnMe(O_2CNR_2)]_4$ (R = *i*Pr and *i*Bu) and $[ZnEt(O_2CN(iPr)_2)]_4$ were recently shown to react with pyridine (py) to give the dinuclear complexes $[(py)ZnMe(O_2CNR_2)]_2$ (R = *i*Pr and *i*Bu) and $[(py)ZnEt(O_2CN(iPr)_2)]_2$.[2,5] Our interest in this area arises from the possibility of using these carbamates as precursors to oxides. Hence we have shown that $[ZnMe(O_2CN(iPr)_2)]_4$ decomposes cleanly at temperatures below 200 °C to give ZnO nanoparticles of an average size of about 10 nm and a pleasingly narrow size distribution.[3]

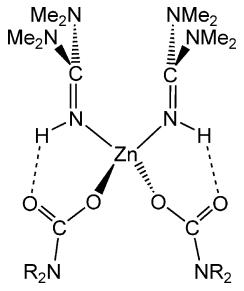
In a preliminary communication we recently reported the synthesis of the first mononuclear Zn complex featuring κ^1-coordinated carbamato ligands, namely $[(tmg)_2Zn(O_2CN(iBu)_2)_2]$ (tmg = *N*,*N*,*N*′,*N*′-tetramethylguanidine, see Scheme 1).[5] In the related complex $[(tmeda)Zn(O_2CNEt_2)_2]$ of the less basic tmeda ligand (tmeda = tetramethylethylenediamine), the two carbamato ligands adopt a κ^2-coordination mode.[6] The change of coordination mode is presumably caused by the instability of the ZnO_2C four-membered ring, which is formed in the case of κ^2-coordination because of the large accumulation of electron den-



Scheme 1.

[a] Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax: +49-6221-545707
E-mail: hans-jorg.himmel@aci.uni-heidelberg.de
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

sity. Quantum chemical calculations fully support this explanation.[5] However, it was not possible from the experimental results alone to judge the structural consequences of N–H···O interactions, which are established between the guanidine and the carbamate (see Scheme 2). Herein we analyse in detail the reaction of the tetranuclear complexes $[ZnEt(O_2CNR_2)]_4$ (R = *i*Pr or *i*Bu) with several nitrogen bases including the three guanidine bases *N*,*N*,*N*′,*N*′-tetramethylguanidine (tmg), bis-*N*,*N*,*N*′,*N*′-tetramethylguanidine naphthalene (btmgn) and bis-*N*,*N*,*N*′,*N*′-tetramethylguanidine benzene (btmgb, see Scheme 1). New carbamato complexes will be shown to emerge from this "top-down" approach.



Scheme 2.

Results and Discussion

We started our study with the reaction between $[Zn(Et)NR_2]_n$ (R = *i*Pr and *i*Bu) and CO_2, which results in the formation of the tetranuclear carbamato complex $[ZnEt(O_2CNR_2)]_4$.[3] This complex can subsequently be treated with a base to give mono-, bi- and trinuclear complexes, depending on the base strength and the relative concentration of the two reactants. In the following, we report in turn on the results obtained with pyridine, tmg, btmgn and btmgb (see Scheme 1).

Reaction of $[ZnEt(O_2CNR_2)]_4$ with Pyridine

As already mentioned, the reaction of other tetrameric alkylzinc carbamate with pyridine was analysed previously[2,5] and was shown to lead to dinuclear Zn complexes featuring two bridging carbamato ligands. Figure 1 illustrates, as a further example, the structure of $[(py)ZnEt(O_2CN(iBu)_2)]_2$ (**1**), representing the product of the reaction of $[ZnEt(O_2CN(iBu)_2)]_4$ with pyridine (py). The structure is similar to those of $[(py)ZnEt(O_2CN(iPr)_2)]_2$[5] and $[(py)ZnMe(O_2CNR_2)]_2$ (R = *i*Pr and *i*Bu).[2] The molecule exhibits a central puckered eight-membered ring. Both Zn atoms are bound to two O atoms, one ethyl C atom and a pyridine N atom. Selected structural parameters are listed in Table S1 of the Supporting Information. In contrast to the results obtained with guanidine derivatives (see below), no other product is formed (even with a very large excess of pyridine), including mono- or trinuclear species.

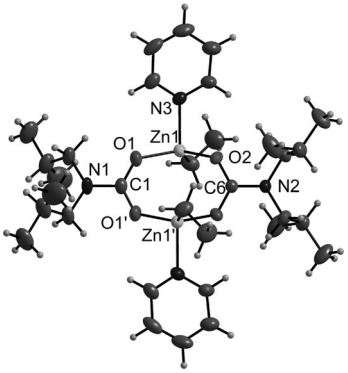


Figure 1. Molecular structure of $[(py)ZnEt(O_2CN(iBu)_2)]_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

Reaction of $[ZnEt(O_2CNR_2)]_4$ with tmg

Reaction between $[ZnEt(O_2CN(iPr)_2)]_4$ and 4 equiv. of tmg yielded the dinuclear complex $[(tmg)ZnEt(O_2CN(iPr)_2)]_2$ (**2**). Its structure is displayed in Figure 2 (see Table S2 in the Supporting Information for selected structural parameters). Again a puckered eight-membered ring is formed and the two tmg ligands as well as the two ethyl groups adopt a *trans* conformation. At 202.8(3) pm the Zn–N distances from the Zn to the directly bound N atom of the tmg ligand in **2** are significantly shorter than the Zn–N distances from the Zn to the pyridine N atoms in **1**. In contrast, the Zn–O distances are shorter in **1** than in **2**. The two complexes also differ in the O–Zn–O angles; in **1** this angle measures 108.11(6)° while in **2** it is only 99.88(8)°. These structural differences are clearly a consequence of the stronger basicity of tmg with respect to pyridine.

In contrast, the reaction between $[ZnEt(O_2CN(iPr)_2)]_4$ and 8 equiv. of tmg proceeded to the mononuclear bis-carbamato complex $[(tmg)_2Zn(O_2CN(iPr)_2)_2]$ (**3**). The molecular structure, as derived from an analysis of the X-ray diffraction data, is visualized in Figure 3. As in the previously reported complex $[(tmg)_2Zn(O_2CN(iBu)_2)_2]$,[5] the two carbamato ligands are κ^1-coordinated. At 196.3 and 195.3 pm, the Zn–O1 and Zn–O3 bond lengths are relatively short. The Zn···O2 and Zn···O4 separations amount to 313.4 and 322.5 pm and show that no significant interactions are established between these atoms. Other structural parameters can be found in Table S3 (Supporting Information). Quantum chemical calculations carried out for the model complexes $[(tmeda)Zn(O_2CNH_2)_2]$ and $[(tmg)_2Zn(O_2CNH_2)_2]$ show that the former exhibits κ^2- and the latter κ^1-coordinated carbamato ligands,[5] in full agreement with the experimental results. The difference in the coordination mode highlights the basicity difference between amine and guanidine bases [the p*K*(BH^+) values in MeCN for tmg and btmgn are 23.3 (13.6 in H_2O)[7] and 25.1,[8] respectively]. There is, however, the possibility of further stabilisation of this structure by N–H···O=C interactions between the carbonyl O atom of the carbamato groups and the H atom attached to the imine N atom in the TMG ligands. Accord-

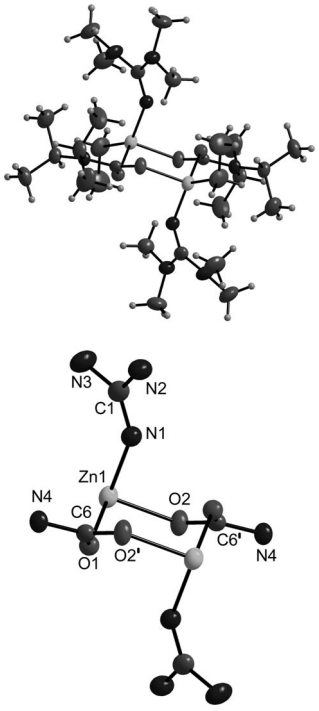


Figure 2. Molecular structure of $[(tmg)EtZn(O_2CN(iPr)_2)]_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level.

ing to the X-ray diffraction analysis, these H···O contacts measure about 214–215 pm [N···O separations of 282.1(2) and 287.0(3) pm] in **3**.

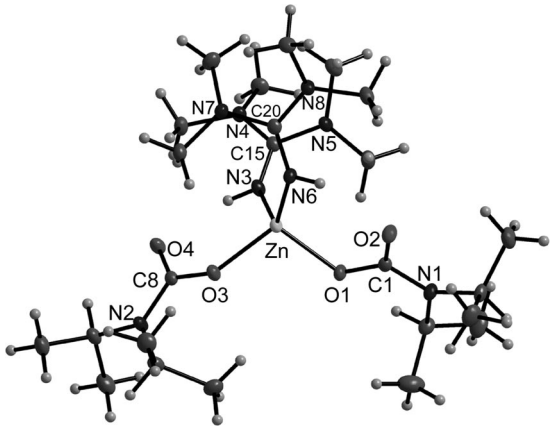


Figure 3. Molecular structure of $[(tmg)_2Zn(O_2CN(iPr)_2)_2]$ (**3**). Thermal ellipsoids are drawn at the 50% probability level.

In all these reactions traces of water have to be excluded rigorously. In the presence of small traces of H_2O (or of the hydroxide salt of the guanidinium cation) in the reaction mixture, other products are formed. Hence reaction between $[ZnEt(O_2CN(iBu)_2)]_4$ and an excess of tmg in the presence of small quantities of water leads to crystals that consist of tetranuclear $[(tmg)_2Zn_4Et_2(O_2CN(iBu)_2)_4O]$ molecules, **4**. The molecular structure of this species is illustrated in Figure 4 and features a central O atom that is coordinated by four Zn atoms in a tetrahedral fashion. All carbamato ligands are κ^2-coordinated. Two of the Zn atoms are further bound to ethyl groups (Zn1 and Zn4) and the others to tmg units (Zn2 and Zn3). On average, the Zn2–O and Zn3–O distances (O from the carbamato ligands) are shorter than the Zn1–O and Zn4–O distances (see Table S4 in the Supporting Information for a list of selected structural parameters).

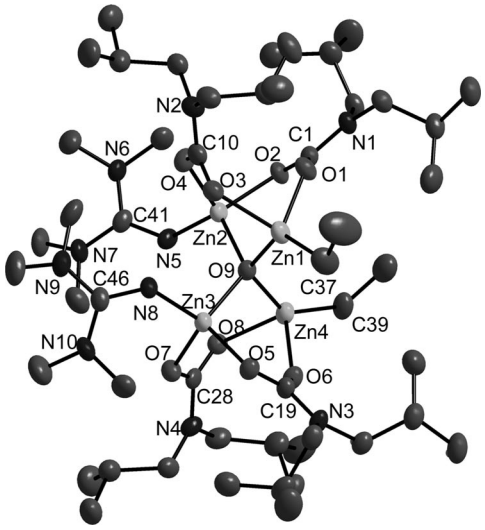


Figure 4. Molecular structure of $[(tmg)_2Zn_4Et_2(O_2CN(iBu)_2)_4O]$ (**4**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for the sake of clarity.

Reaction of $[ZnEt(O_2CNR_2)]_4$ with btmgn

Further experiments were carried out with the chelating bisguanidine btmgn. Reaction between $[ZnEt(O_2CN(iPr)_2)]_4$ and 4 equiv. of btmgn leads to the mononuclear complex $[(btmgn)ZnEt(O_2CN(iPr)_2)]$ (**5**). Crystals suitable for X-ray diffraction were grown from toluene solutions at –20 °C. Figure 5 displays the obtained molecular structure (see Table S5 of the Supporting Information for selected structural parameters). Most importantly, the carbamato ligand is κ^1-coordinated, as in complex **3**. In this case there is no possibility for hydrogen bonding from the guanidine ligand to the carbonyl O atom of the carbamato ligand. The structure thus confirms that indeed the stronger basicity of the guanidine is responsible for the change in the carbamato coordination mode. The Zn–O distance in **5** [198.7(4) pm] is slightly larger than the Zn–O distances in **3** [196.3(1) and 195.3(1) pm]. As already observed in the case of complexes of group 10 metals with btmgn ligands,[9] the metal is not located in the plane defined by the naphthalene aromatic system. Hence in **5** the Zn atom is 122.0 pm above this plane. However, in contrast to the Pd and Pt complexes $[(btmgn)PdCl_2]$ and $[(btmgn)PtCl_2]$,[9] the naphthyl system in **5** remains planar. At 206.0(7) and 207.4(7) pm, the two Zn–N distances from the Zn to the directly bound N atoms of the btmgn ligand are relatively large. For comparison, the two Zn–N distances from the Zn to the two directly bound N atoms of the tmg ligands in **3** are below 200 pm

[199.7.4(1) and 198.7(1) pm]. It is noteworthy in this context that in the crystalline phase the carbamato unit and not the ethyl group is located between the two guanidine units of the btmgn ligand (see Figure 5). At first glance it is surprising that no disproportionation and formation of [(btmgn)-$Zn(O_2CNR_2)_2$] is observed, in sharp contrast to the reaction with tmg. The btmgn ligand is less flexible than the two tmg ligands, so that steric constraints are most likely the reason for this difference. The carbamato ligand is sterically more demanding than the ethyl group. To the best of our knowledge, complex **5** represents the first example of a structurally characterized monomeric alkylzinc carbamate. These species usually tend to form oligomers, like the $[ZnEt(O_2CNR_2)]_4$ tetramers (R = *i*Pr and *i*Bu) used in this work. The complex is also quite stable compared to the related [(btmgn)$ZnEt_2$] complex.[10]

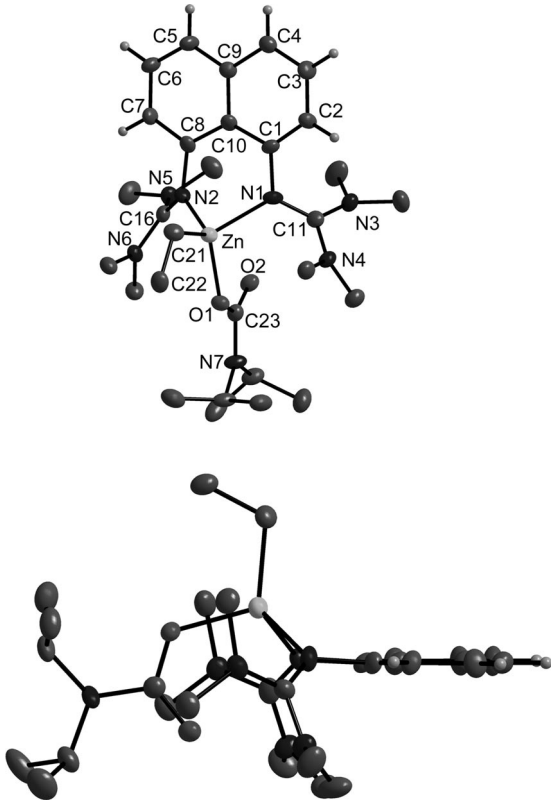


Figure 5. Molecular structure of [(btmgn)ZnEt($O_2CN(iPr)_2$)] (**5**) from two different perspectives. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the Me, Et and *i*Pr groups were omitted for the sake of clarity.

We also obtained the complex [(btmgn)ZnEt(O_2CN-($iBu)_2$)] (**6**) from the reaction between [$ZnEt(O_2CN$-($iBu)_2)]_4$ and btmgn. Crystals were grown from toluene solution and contained solvent molecules. The elemental cell contains two slightly different molecules of **6**. The structure of one of the molecules is depicted in Figure 6. Selected structural data are listed in Table S6 (Supporting Information). As anticipated, the structure is similar to that of **5**.

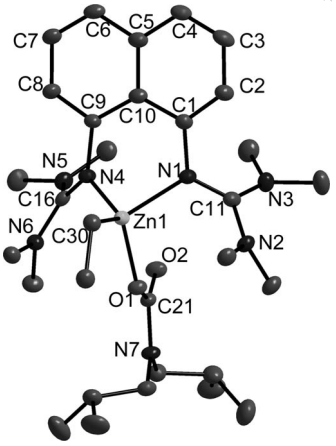
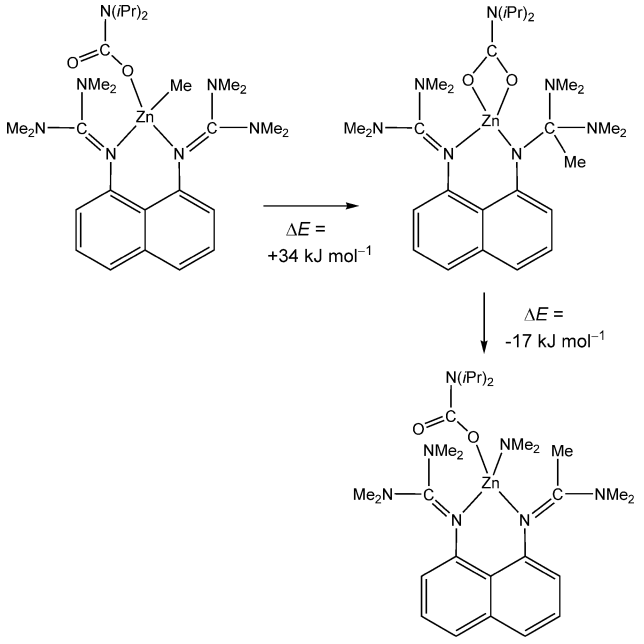


Figure 6. Molecular structure of [(btmgn)ZnEt($O_2CN(iBu)_2$)] (**6**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for the sake of clarity.

Monomeric Zn–alkyl complexes are known to be alkyl transfer reagents. In particular, the transfer of an alkyl group in [(R′dab)ZnR_2] complexes (R′dab = 1,4-disubstituted 1,4-diaza-1,3-butadiene, R′N=CH–CH=NR′) from the Zn atom to the R′dab ligand by a single electron transfer (SET) process has been extensively studied in the past.[11] Like the R′dab ligand, the guanidinyl groups of the btmgn ligand feature C=N double bonds, which in principal could be alkylated. The question therefore arises whether the alkyl group in [(btmgn)ZnR($O_2CN(iPr)_2$)] can be transferred to the bisguanidine ligand. Quantum chemical (DFT) calculations were carried out with R = Me prior to experimental work to test the energetics for this transformation and to obtain information about the likely structure of the product. According to BP86/SV(P), alkyl transfer to the C atoms of the C=N imine bond within one guanidinyl group (see Scheme 3) is associated with an energy of +34 kJ mol^{-1}. Table S7 (Supporting Information) compares some structural parameters as calculated for the starting complex and the possible alkylation product. From Table 1 one can also see that the calculated structure for the starting complex is in good agreement with the experimentally determined structure. Interestingly, the energy change for a hypothetical second process, a transfer of one of the NMe_2 groups of the alkylated group to the Zn and restoration of the C=N double bond yielding a mixed guanidine-aminidine ligand, is calculated to be negative (–17 kJ mol^{-1}).

NMR spectra were recorded for toluene solutions of [(btmgn)ZnEt($O_2CN(iBu)_2$)] at various temperatures to search for possible experimental evidence of an alkyl transfer and also to evaluate the fluxional processes within the complex, especially within the guanidinyl ligand. The NMR spectra gave no sign of an alkylation, even at 80 °C. At this temperature the methyl groups of the btmgn ligand give a single broad signal around 2.6 ppm in the ^{1}H NMR spectra, indicating fast fluxional processes on the NMR timescale. Irradiation with broad-band light also produced no changes in the NMR spectra. Thus alkylation does not occur.



Scheme 3.

Table 1. Comparison between calculated [BP/SV(P)] structural parameters (distances in pm, angles in °) before and after (hypothetical) alkylation of the btmgn ligand by transfer of methyl from the Zn atom in [(btmgn)ZnMe($O_2CN(iPr)_2$)] to the ligand (see Figure 5 and Figure S1 for atom numbering).

	Before alkylation		After alkylation
	Exp.	Calcd.	Calcd.
Zn–C	200.4	200.1	
Zn–O1	198.7	202.9	206.9
Zn–O2	309.5	325.6	210.5
Zn–N1	206.0	212.0	202.4
Zn–N2	207.4	212.5	194.1
N1–C1	141.7	140.7	142.7
N1–C11	132.5	133.5	133.0
C11–N3	137.9	138.3	138.3
C11–N4	133.6	137.1	137.9
N2–C8	142.1	141.0	139.0
N2–C16	130.7	133.1	147.8
C16–N5	136.8	138.5	148.8
C16–N6	134.6	137.3	149.7
N1–Zn–N2	86.1	84.1	92.5
O1–C–O2	125.7	125.5	118.8
O1–Zn–O2			64.5

Finally, we obtained the trinuclear species [(btmgn)$Zn_3Et_3(O_2CN(iPr)_2)_3$] (**7**) by reaction of [$ZnEt(O_2CN(iPr)_2)]_4$ with 2 equiv. of btmgn. Figure 7 displays its molecular structure. Selected structural parameters are listed in Table S7 (Supporting Information). The complex can be described as a Lewis acid-base complex between [$ZnEt(O_2CN(iPr)_2)]_2$ and **5**. It is therefore most likely formed by reaction between **5** and remaining oligonuclear ethylzinc carbamate species in the solution. To test this hypothesis we treated compound **5** with [$ZnEt(O_2CN(iPr)_2)]_4$ in a 2:1 molar ratio. The NMR spectra indeed indicated formation of **7**. Similar to the situation in **5**, the Zn atom is dislocated (by 85.5 pm in this case) from the plane defined by the naphthalene aromatic system. The carbamate unit connecting the mononuclear part with the dinuclear part of the complex adopts a $\kappa^{1,2}O$-κ^3O' coordination mode. As anticipated, the Zn3–O6 bond is significantly shorter than the Zn1–O5 and Zn2–O5 bonds, in agreement with the bonding situation in [$ZnEt(O_2CN(iPr)_2)]_4$, also featuring $\kappa^{1,2}O$-κ^3O' coordinated carbamato ligands.

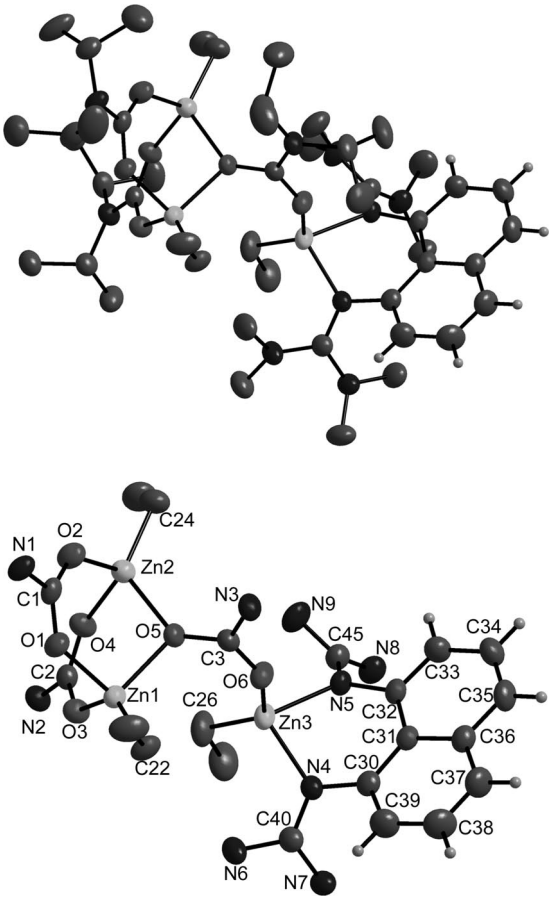


Figure 7. Molecular structure of [(btmgn)$Zn_3Et_3(O_2CN(iPr)_2)_3$] (**7**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms of the Me, Et and *i*Pr groups were omitted for the sake of clarity.

Reaction of [$ZnEt(O_2CNR_2)]_4$ with btmgb

Reaction between [$ZnEt(O_2CNR_2)]_4$ and 2 equiv. of btmgb also resulted in formation of a single product. However, we were unfortunately unable to crystallize this species. Nevertheless, the NMR spectra (see Exp. Section) are in agreement with its formulation as the equivalent to **5**, namely the mononuclear complex [(btmgb)$ZnEt(O_2CN(iBu)_2)$] (**8**).

Conclusions

This work deals with reactions between tetrameric alkylzinc carbamates and various nitrogen bases [namely pyridine (py) and the three guanidine bases *N*,*N*,*N*′,*N*′-tet-

ramethylguanidine (tmg), bis-*N*,*N*,*N*′,*N*′-tetramethylguanidine naphthalene (btmgn) and bis-*N*,*N*,*N*′,*N*′-tetramethylguanidine benzene (btmgb)]. It is shown that following a top-down synthetic approach, new carbamato-Zn complexes of different sizes can be prepared by these reactions. Hence we report on the synthesis and structural characterization of the mononuclear species $[(tmg)_2Zn(O_2CNR_2)_2]$ and $[(btmgn)ZnEt(O_2CNR_2)]$, the dinuclear complexes $[(py)Zn(O_2CNR_2)]_2$ and $[(tmg)Zn(O_2CNR_2)]_2$, and the trinuclear complex $[(btmgn)Zn_3Et_3(O_2CNR_2)_3]$ (R = *i*Pr and/or *i*Bu). In contrast to the tmeda-stabilized mononuclear carbamato complex, the mononuclear complexes with guanidine bases feature κ^1-coordinated carbamato ligands. Among these, the two complexes $[(btmgn)ZnEt(O_2CN(iPr)_2)]$ and $[(btmgn)ZnEt(O_2CN(iBu)_2)]$ are especially noteworthy for being the first structurally characterized monomeric carbamato-alkylzinc complexes. Figure 8 summarizes the reactions that were studied in this work using the bases py, tmg and btmgn.

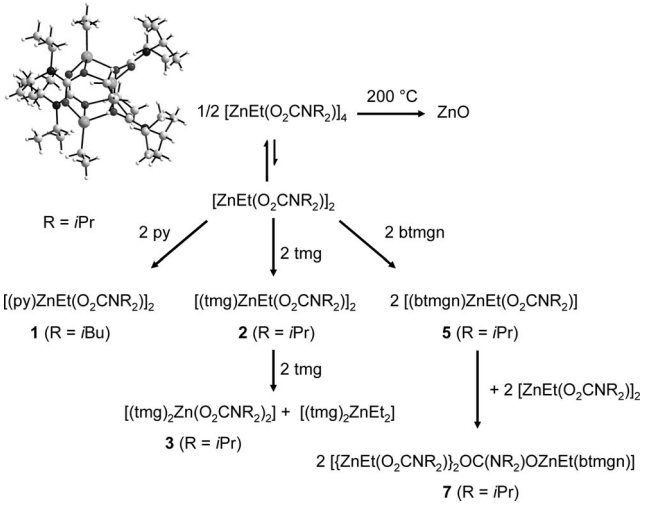


Figure 8. Reaction pathways for reaction of tetranuclear alkylzinc carbamates with the three nitrogen bases pyridine, tmg and btmgn.

We are currently exploring the chemical properties of these new complexes, one of the main issues being the preparation of heteronuclear carbamates (especially ones containing Co) using Zn complexes as building blocks. These carbamates might be interesting precursors for the fabrication of new functional (magnetic) materials.[3]

Experimental Section

General: All reactions were carried out under dry argon using standard Schlenk techniques. All solvents were dried using standard methods followed by distillation. Pyridine as well as the two guanidine bases *N*,*N*,*N*′,*N*′-tetramethylguanidine (tmg) and bis(*N*,*N*,*N*′,*N*′-tetramethylguanidinyl)naphthalene (btmgn) were purchased from Aldrich. Bis(*N*,*N*,*N*′,*N*′-tetramethylguanidinyl)-benzene (btmgb) was synthesized as described in the literature.[12,13] $[ZnEt(O_2CNR_2)]_4$ (R = *i*Pr or *i*Bu) was prepared from $ZnEt_2$ and the corresponding secondary amine as described in the literature.[3] NMR spectra were measured with a Bruker Avance II 400 and an AC200 spectrometer. A BIORAD Excalibur FTS 300 spectrometer was used for the IR spectra (see Supporting Information).

$[(py)ZnEt(O_2CN(iBu)_2)]_2$ (1): $[ZnEt(O_2CN(iBu)_2)]_4$ (0.28 g, 0.26 mmol) was dissolved in toluene (10 mL), treated with an excess of pyridine (1 mL) and stirred for 3 h. The solution was then evaporated to dryness and the solid product recrystallized from hexane at –20 °C to give colourless crystals of $[ZnEt(O_2CN(iBu)_2)(py)]_2$ (0.29 g, 0.42 mmol, 81%). $C_{32}H_{56}N_4O_4Zn_2$ (691.58): calcd. C 55.57, H 8.16, N 8.10; found C 54.69, H 8.04, N 8.08. ^{1}H NMR (400 MHz, C_6D_6): δ = –0.16 (q, ^3J = 8.00 Hz, 4 H, CH_3CH_2Zn), 0.91 (d, ^3J = 6.40 Hz, 24 H, Me_2CHCH_2), 1.48 (t, ^3J = 8.04 Hz, 6 H, CH_3CH_2Zn), 2.04 (m, ^3J = 6.84 Hz, 4 H, Me_2CHCH_2), 3.19 (d, ^3J = 7.20 Hz, 8 H, Me_2CHCH_2), 6.64 (t, ^3J = 5.80 Hz, 4 H, py), 6.93 (t, ^3J = 7.52 Hz, 2 H, py), 8.55 (d, ^3J = 4.40 Hz, 4 H, py) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ = –1.34 (CH_3CH_2Zn), 13.79 (CH_3CH_2Zn), 20.51 (Me_2CHCH_2), 27.64 (Me_2CHCH_2), 55.49 (Me_2CHCH_2), 123.73 (py), 135.97 (py), 150.04 (py), 165.19 (CO_2) ppm. IR (KBr): $\tilde{\nu}$ = 1560, 1499 [ν(CO)] cm^{-1}.

$[(tmg)ZnEt(O_2CN(iPr)_2)]_2$ (2): $[ZnEt(O_2CN(iPr)_2)]_4$ (1 g, 1 mmol) was dissolved in toluene (10 mL) and treated with 4 equiv. of tmg (0.51 mL, 4 mmol) for 2 h at room temperature under argon. The solution was then evaporated to dryness and the solid product recrystallized from toluene at 10 °C to give colourless cubic crystals (0.55 g, 0.78 mmol, 39%). $C_{28}H_{62}N_8O_4Zn_2$ (705.64): calcd. C 47.66, H 8.86, N 15.88; found C 46.78, H 8.87, N 16.08. ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 0.58 (q, ^3J = 8.08 Hz, 2 H, CH_3CH_2Zn), 1.79 (t, ^3J = 8.02 Hz, 3 H, CH_3CH_2Zn), 1.28 (d, ^3J = 6.71 Hz, 12 H, Me_2CH), 2.39 (s, 6 H, Me_2N), 2.62 (s, 6 H, Me_2N), 4.05 (m, ^3J = 6.63 Hz, 2 H, Me_2CH), 6.15 (b, 1 H, *NH*) ppm. ^{13}C NMR (50.27 MHz, [D$_8$]toluene): δ = 0.62 (CH_3CH_2Zn), 14.26 (CH_3CH_2Zn), 21.65 (Me_2CH), 38.73 (-NMe_2), 39.28 (-NMe_2), 45.59 (-CHMe$_2$), 163.27 (CO_2), 166.94 [N=C(NMe$_2$)$_2$] ppm. IR (CsI): $\tilde{\nu}$ = 1605, 1560 [ν(CO)] cm^{-1}.

$[(tmg)_2Zn(O_2CN(iPr)_2)_2]$ (3): $[ZnEt(O_2CN(iPr)_2)]_4$ (0.6 g, 0.63 mmol) was dissolved in toluene (5 mL) and hexane (1 mL) and treated with 8 equiv. of tmg (0.65 mL, 5.04 mmol) for 24 h at room temperature under argon. The solution was then evaporated to dryness and the solid product recrystallized from toluene/hexane (1:1) at 10 °C to give colourless cubic crystals (0.30 g, 0.51 mmol, 40%). $C_{24}H_{54}N_8O_4Zn$ (584.12): calcd. C 49.34, H 9.34, N 19.18; found C 48.19, H 8.89, N 17.68.[14] ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 1.23 (^3J = 6.77 Hz), 1.40 (d, ^3J = 6.77 Hz, 24 H, Me_2CH), 2.35 (s, 12 H, Me_2N), 2.73 (s, 12 H, Me_2N), 3.95 (m, ^3J = 6.65 Hz, 2 H, -CHMe$_2$), 4.2 (m, ^3J = 6.75 Hz, 2 H, -CHMe$_2$), 6.73 (b, 2 H, *NH*) ppm. ^{13}C NMR (50.27, [D$_8$]toluene): δ = 21.33 (Me_2CH), 22.07 (Me_2CH), 38.83 (-NMe_2), 39.39 (-NMe_2), 45.20 (-CHMe$_2$), 45.86 (-CHMe$_2$), 162.53 (CO_2), 163.14 (CO_2), 167.22 [N=C(NMe$_2$)$_2$] ppm. IR (CsI): $\tilde{\nu}$ = 1606, 1564 [ν(CO)] cm^{-1}.

$[(tmg)_2Zn_4Et_2(O_2CN(iBu)_2)_2O]$ (4): The procedure was similar to that used for compound **3**. The compound was obtained in the presence of small amounts of water in the reaction mixture. ^{1}H NMR (200 MHz, C_6D_6): δ = 0.67 (q, ^3J = 8.00 Hz, 2 H, CH_3CH_2Zn), 0.96 (d, ^3J = 6.80 Hz, 12 H, Me_2CHCH_2), 1.89 (t, ^3J = 8.00 Hz, 3 H, CH_3CH_2Zn), 2.11 (m, ^3J = 7.00 Hz, 2 H, Me_2CHCH_2), 2.32/2.57 (s, 12 H, NMe_2), 3.29 (d, ^3J = 7.40 Hz, 4 H, Me_2CHCH_2) ppm. ^{13}C NMR (50.27 MHz, C_6D_6): δ = 0.98 (CH_3CH_2Zn), 14.27 (CH_3CH_2Zn), 20.71 (Me_2CHCH_2), 27.93 (Me_2CHCH_2), 38.73/39.30 (NMe_2), 55.62 (Me_2CHCH_2), 164.97 (CO_2), 166.95 [N=C(NMe$_2$)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 1600, 1562 [ν(CO)] cm^{-1}.

$[(btmgn)ZnEt(O_2CN(iPr)_2)]$ (5): $[EtZn(O_2CN(iPr)_2)]_4$ (0.1 g, 0.1 mmol) was dissolved in toluene (3 mL) and treated with 4 equiv. of

btmgn (0.142 g, 0.4 mmol) for 24 h at room temperature under argon. The solution was then evaporated to dryness and the solid product recrystallized from toluene at –20 °C to give colourless needle-shaped crystals (0.044 g, 0.074 mmol, 19%). $C_{29}H_{49}N_7O_2Zn$ (593.12): calcd. C 58.78, H 8.28, N 16.55; found C 58.82, H 8.24, N 16.48. ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 0.44 (q, ^3J = 8.09 Hz, 2 H, CH_3CH_2Zn), 1.36 (d, ^3J = 6.77 Hz, 12 H, Me_2CH), 1.54 (t, ^3J = 8.09 Hz, 3 H, CH_3CH_2Zn), 2.22/2.26 (s, 12 H, Me_2N), 2.75/3.21 (s, 12 H, Me_2N), 4.15 (m, 2 H, $CHMe_2$), 6.24 [dd, ^3J(H4H3) = 7.43, ^4J(H4H2) = 0.89 Hz, 2 H, H4,5], 7.19 [t, ^3J(H3H4) = 7.75, ^3J(H3H2) = 7.75 Hz, 2 H, H3,6], 7.41 [dd, ^3J(H2H3) = 8.19, ^4J(H2H4) = 0.89 Hz, 2 H, H2,7] ppm. ^{13}C NMR (50.27 MHz, [D$_8$]toluene): δ = 1.15 (CH_3CH_2Zn), 14.81 (CH_3CH_2Zn), 22.57 (Me_2CH), 39.34 (-NMe_2), 44.86 (-CHMe$_2$), 117.68, 122.70, 125.74, 148.21, 150.36 (aromat. C), 160.96 (CO2), 164.38 [N=C(NMe$_2$)$_2$] ppm. IR (CsI): $\tilde{\nu}$ = 1587, 1549 [ν(CO)] cm^{-1}.

[(btmgn)ZnEt(O$_2$CN(iBu)$_2$)] (6): [EtZn(O$_2$CN(iBu)$_2$)]$_4$ (0.50 g, 0.47 mmol) was dissolved in toluene (5 mL) and treated with a toluene (4 mL) solution of 4 equiv. of btmgn (0.67 g, 1.88 mmol) for 24 h at room temperature under argon. The solution was then evaporated to dryness and the solid product recrystallized from toluene at –20 °C to give colourless crystals (0.96 g, 1.54 mmol, 82%). $C_{31}H_{53}N_7O_2Zn$ (621.19): calcd. C 59.94, H 8.60, N 15.78; found C 60.85, H 8.58, N 15.37. ^{1}H NMR (600 MHz, [D$_8$]toluene): δ = 0.33 (q, ^3J = 8.07 Hz, 2 H, CH_3CH_2Zn), 0.96 (d, ^3J = 6.64 Hz, 12 H, Me_2CHCH_2), 1.45 (t, ^3J = 8.07 Hz, 3 H, CH_3CH_2Zn), 2.11 (br., 2 H, Me$_2CH$CH$_2$), 2.16 (s, 12 H, Me_2N), 2.64/3.08 (s, 12 H, Me_2N), 3.19 (d, ^3J = 7.04 Hz, 4 H, Me$_2$CHCH_2), 6.12 [d, ^3J(H4H3) = 7.36 Hz, 2 H, H4,5], 7.08 (t, ^3J = 7.73 Hz), 7.30 [d, ^3J(H2H3) = 8.13 Hz, 2 H, H2,7] ppm. ^{13}C NMR (151 MHz, [D$_8$]toluene): δ = 1.36 (CH_3CH_2Zn), 14.70 (CH_3CH_2Zn), 21.29 (Me_2CHCH_2), 28.91 (Me$_2CH$CH$_2$), 38.84/39.48/41.52 (Me_2N), 57.89 (Me$_2$CHCH_2), 117.70/122.76/125.84/129.26/138.35/148.19 (C_{Ar}), 162.44 (CO_2), 164.56 [N=C(NMe$_2$)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 1599, 1555 [ν(CO)] cm^{-1}.

[(btmgn)Zn$_3$Et$_3$(O$_2$CN(iPr)$_2$)$_3$] (7): [ZnEt(O$_2$CN(iPr)$_2$)]$_4$ (0.1 g, 0.1 mmol) was dissolved in toluene (3 mL) and hexane (1 mL) and treated with 2 equiv. of btmgn (0.071 g, 0.2 mmol) for 24 h at room temperature under argon. The solution was then evaporated to dryness and the solid product recrystallized from toluene hexane 4:1 at 10 °C to give colourless cubic crystals (0.07 g, 0.061 mmol, 31%). $C_{47}H_{87}N_9O_6Zn_3$ (1070.40): calcd. C 52.74, H 8.19, N 11.78; found C 49.25, H 7.40, N 9.07.[14] ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = –0.02 (q, ^3J = 7.76 Hz, 2 H, CH_3CH_2Zn), 0.45 (q, ^3J = 8.06 Hz, 4 H, CH_3CH_2Zn), 0.94 (t, ^3J = 7.20 Hz, 3 H, CH_3CH_2Zn), 1.18 (d, ^3J = 6.77 Hz, 27 H, Me_2CH), 1.36 (d, ^3J = 6.78 Hz, 9 H, $Me2CH$), 1.45 (t, ^3J = 8.12 Hz, 6 H, CH_3CH_2Zn), 2.61 (s, 24 H, Me_2N), 3.92 (m, ^3J = 6.78 Hz, 4 H, $CHMe_2$), 4.06 (b, 2 H, $CHMe_2$), 6.49 [dd, ^3J(H4-H3) = 7.24, ^4J(H4-H2) = 0.99 Hz, 2 H, H4,5], 7.31 [dd, ^3J(H3H4) = 7.34, ^3J(H3H2) = 8.01 Hz, 2 H, H3,6], 7.44 [dd, ^3J(H2-H3) = 8.18, ^4J(H2H4) = 0.90 Hz, 2 H, H2,7] ppm. ^{13}C NMR (50.27 MHz, [D$_8$]toluene): δ = 0.01 (CH_3CH_2Zn), 1.38 (CH_3CH_2Zn), 11.67 (CH_3CH_2Zn), 14.14 (CH_3CH_2Zn), 21.03 (Me_2CH), 39.65 (-NMe_2), 46.09 (-CHMe$_2$), 115.79, 120.78, 126.03, 148.04, 153.96, 157.50 (C_{Ar}), 162.84 (CO_2), 169.11 [N=C(NMe$_2$)$_2$] ppm. IR (CsI): $\tilde{\nu}$ = 1553, 1485 [ν(CO)] cm^{-1}.

[(btmgb)ZnEt(O$_2$CN(iBu)$_2$)] (8): btmgb (0.61 g, 2 mmol) in toluene (5 mL) was added dropwise to a toluene (5 mL) solution of [ZnEt{O$_2$CN(iBu)$_2$}]$_4$ (0.53 g, 0.5 mmol). The solution was stirred at room temperature for 18 h. Subsequently the solvent was removed in vacuo and the residue solved in hexane. A white precipitate was obtained at –20 °C. ^{1}H NMR (400 MHz, [D$_8$]toluol): δ =

Table 2. Crystal data and refinement details for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{32}H_{56}N_4O_4Zn_2$	$C_{28}H_{62}N_8O_4Zn_2$	$C_{24}H_{54}N_8O_4Zn$	$C_{50}H_{108}N_{10}O_9Zn_4$
M_r [g mol^{-1}]	1383.10	705.64	584.12	1254.94
Crystal size [mm]	0.40 × 0.40 × 0.30	0.40 × 0.40 × 0.30	0.20 × 0.14 × 0.06	0.30 × 0.30 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	17.370(4)	9.2800(19)	11.6812(11)	17.018(3)
b [Å]	13.660(3)	19.420(4)	13.6524(12)	13.062(3)
c [Å]	17.767(4)	10.422(2)	20.2283(18)	29.230(6)
α [°]				
β [°]	118.51(3)	93.41(3)	102.741(2)	93.51(3)
γ [°]				
V [Å^3]	3704.4(18)	1874.9(7)	3146.5(5)	6485(2)
$\rho_{calcd.}$ [g cm^{-3}]	1.240	1.250	1.233	1.285
Z	4	2	4	4
F(000)	1472	756	1264	2680
hkl range	–22 ≤ h ≤ 22, –17 ≤ k ≤ 17, –23 ≤ l ≤ 23	–12 ≤ h ≤ 12, –25 ≤ k ≤ 25, –13 ≤ l ≤ 13	17 ≤ h ≤ 17, –20 ≤ h ≤ 19, –29 ≤ h ≤ 29	–22 ≤ h ≤ 22, –16 ≤ k ≤ 11, –37 ≤ l ≤ 37
θ range [°]	2.61–27.50	2.10–27.45	1.86–31.80	1.71–27.51
μ [mm^{-1}]	1.331	1.319	0.821	1.515
Measured reflections	8385	8394	79900	23456
Unique reflections (R_{int})	4251 (0.0214)	4268 (0.0434)	10563 (0.0551)	14514 (0.0670)
Observed reflections [$I > 2\sigma(I)$]	3378	3074	7822	8762
Refined parameters/restraints	257/4	199/0	358/0	684/0
Goodness-of-fit	1.040	1.045	1.073	1.011
R_1 [$I > 2\sigma(I)$]	0.0319	0.0488	0.0357	0.0625
wR_2 (all data)	0.0850	0.1206	0.0981	0.1704
Residual electron density [e Å^{-3}] (max./min.)	0.438/–0.460	0.776/–0.443	0.744/–0.314	0.626/–0.554

Table 3. Crystal data and refinement details for compounds **5**–**7**.

	5	**6**	**7**
Empirical formula	$C_{29}H_{49}N_7O_2Zn$	$C_{31}H_{53}N_7O_2Zn{\cdot}0.35C_7H_8$	$C_{47}H_{87}N_9O_6Zn_3{\cdot}0.8C_7H_8$
M_r [g mol^{-1}]	593.12	653.42	1144.07
Crystal size [mm]	0.17 × 0.16 × 0.15	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.20
Crystal system	tetragonal	monoclinic	monoclinic
Space group	$I\bar{4}$	$C2/c$	$C2/c$
a [Å]	23.861(3)	35.750(7)	21.446(4)
b [Å]	23.861(3)	11.986(2)	15.867(3)
c [Å]	12.0663(17)	35.141(7)	36.361(8)
α [°]			
β [°]		90.17(3)	94.04(3)
γ [°]			
V [Å^3]	6870.1(16)	15058(5)	12342(4)
$\rho_{calcd.}$ [g cm^{-3}]	1.147	1.153	1.231
Z	8	16	8
F(000)	2544	5624	4880
hkl range	$-28 \le h \le 28$, $0 \le k \le 28$, $0 \le l \le 14$	$-50 \le h \le 50$, $-17 \le k \le 16$, $-49 \le l \le 50$	$-29 \le h \le 29$, $-21 \le k \le 21$, $-49 \le l \le 49$
θ range [°]	1.89–25.08	1.79–30.54	1.60–29.00
μ [mm^{-1}]	0.748	0.689	1.207
Measured reflections	57156	107712	104515
Unique reflections (R_{int})	6128 (0.1263)	22620 (0.0796)	16341 (0.0608)
Observed reflections [$I > 2\sigma(I)$]	4423	22620	11313
Refined parameters/restraints	366/0	817/0	713/0
Goodness-of-fit	1.082	1.014	1.049
R_1 [$I > 2\sigma(I)$]	0.0594	0.0789	0.0461
wR_2 (all data)	0.1123	0.2460	0.1564
Residual electron density [e Å^{-3}] (max./min.)	1.679/–0.638	1.344/–1.096	0.551/–0.537

0.46 (br., 2 H, CH_3CH_2Zn), 0.94 (d, ^3J = 6.80 Hz, 12 H, Me_2CHCH_2), 1.65 (t, ^3J = 8.00 Hz, 3 H, CH_3CH_2Zn), 2.09 (m, ^3J = 6.80 Hz, 2 H, Me_2CHCH_2), 2.52 (s, 24 H, NMe_2), 3.25 (d, ^3J = 7.20 Hz, 4 H, Me_2CHCH_2), 6.35 (m, 2 H, CH_{Ar}), 6.80 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (101 MHz, [D$_8$]toluol): δ = 2.11 (CH_3CH_2Zn), 14.27 (CH_3CH_2Zn), 20.87 (Me_2CHCH_2), 28.17 (Me_2CHCH_2), 39.56 (NMe_2), 56.00 (Me_2CHCH_2), 119.80 (CH_{Ar}), 121.15 (CH_{Ar}), 142.41 ($C_{Ar}N$=C), 163.36 (CO_2), 165.27 [N=C(NMe$_2$)$_2$] ppm.

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil and fixed on top of a glass capillary. Intensity data were measured at low temperature (200 K) on Nonius Kappa-CCD (complexes **1**–**4** and **6**–**7**) and Bruker AXS Smart-1000 diffractometers (**5**, 100 K) using graphite-monochromated Mo-K_α radiation. The data collected were processed using the standard Nonius and Bruker software.[15] Intensity statistics for complex **5** were heavily in favour of a noncentrosymmetric space group. The structure could however be solved in both $I\bar{4}$ and $I4/m$. Refinement in $I4/m$ was unstable and did not converge. The data were therefore treated as an inversion twin in $I\bar{4}$ with a refined batch scale factor of 0.46(2). All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[16,17] Graphical handling of the structural data during solution and refinement was performed with XPMA.[18] Structural representations were generated using *Winray* 32.[19] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations. Tables 2 and 3 contain information on the crystals of compounds **1**–**7**.

CCDC-697644 (for **1**), -697645 (for **2**), -697646 (for **3**), -697647 (for **4**), -697648 (for **5**), -697649 (for **6**) and -707182 (for **7**) 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.

Quantum Chemical Calculations: DFT calculations were carried out with the help of the TURBOMOLE program.[20] The BP86 functional[21] in combination with an SV(P) basis set[22] was applied. The Supporting Information contains the optimized coordinates and SCF energies.

Supporting Information (see also the footnote on the first page of this article): Selected bond lengths (pm) and angles (°) from X-ray diffraction measurements for compounds **1**–**7**, illustration of the calculated structure of the product of methyl transfer from the Zn atom to the btmgn ligand starting from [(btmgn)ZnMe(O_2CN(iPr)$_2$)], IR spectra for **1**–**7**, and calculated SCF energies and coordinates for isomers of [(btmgn)ZnMe(O_2CN(iPr)$_2$)].

Acknowledgments

The authors gratefully acknowledge continuous financial support by the Deutsche Forschungsgemeinschaft (DFG).

[1] I. Abrahams, M. A. Malik, M. Motevalli, P. O'Brien, *J. Chem. Soc., Dalton Trans.* **1995**, 1043–1046.
[2] Y. Tang, W. S. Kassel, L. N. Zakharov, A. L. Rheingold, R. A. Kemp, *Inorg. Chem.* **2005**, *44*, 359–364.
[3] D. Domide, E. Kaifer, J. Mautz, O. Walter, S. Behrens, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2008**, 3177–3185.
[4] H.-J. Himmel, *Eur. J. Inorg. Chem.* **2007**, 675–683.
[5] C. Neuhäuser, D. Domide, J. Mautz, E. Kaifer, H.-J. Himmel, *Dalton Trans.* **2008**, 1821–1824.
[6] M. A. Malik, M. Motevalli, P. O'Brien, *Inorg. Chem.* **1995**, *34*, 6223–6225.

[7] R. Schwesinger, *Nachr. Chem. Tech. Lab.* **1990**, *38*, 1214–1226; and references given therein.
[8] V. Raab, J. Kipke, R. M. Gschwind, J. Sundermeyer, *Chem. Eur. J.* **2002**, *8*, 1682–1693.
[9] U. Wild, O. Hübner, A. Maronna, M. Enders, E. Kaifer, H. Wadepohl, H.-J. Himmel, *Eur. J. Inorg. Chem.* **2008**, 4440–4447.
[10] U. Wild, M. Reinmuth, E. Kaifer, H.-J. Himmel, unpublished results.
[11] See, for example: a) M. Kaupp, H. Stoll, H. Preuss, W. Kaim, T. Stahl, G. Van Koten, E. Wissing, W. J. J. Smeets, A. L. Spek, *J. Am. Chem. Soc.* **1991**, *113*, 5606–5618; b) 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.
[12] M. Kawahata, K. Yamaguchi, T. Ito, T. Ishikawa, *Acta Crystallogr., Sect. E* **2006**, *E62*, o3301–o3302.
[13] A. Peters, U. Wild, O. Hübner, E. Kaifer, H.-J. Himmel, *Chem. Eur. J.* **2008**, *14*, 7813–7821.
[14] The following reasons can be given for the deviations of the elemental analysis data from the expectation in the case of compounds **3** and **7**: (i) Solid **3** most likely contains minor impurities of **2** or its monomeric form, which cannot be eliminated. (ii) Compound **7** represents a (relatively weakly bound) complex between **5** and $[ZnEt(O_2CN(i\text{Pr})_2)]_2$, and the solid most likely contains a small excess of the latter or its dimer (the starting compound).
[15] a) *DENZO-SMN*, Data processing software, Nonius, **1998**; http://www.nonius.com; b) *SAINT*, Bruker AXS, **2007**; G. M. Sheldrick, *SADABS*, Bruker AXS, **2004**–**2008**.
[16] a) G. M. Sheldrick, *SHELXS-97*, *Program for Crystal Structure Solution*, University of Göttingen, Göttingen, **1997**; http://shelx.uni-ac.gwdg.de/SHELX/index.html; b) G. M. Sheldrick, *SHELXL-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, **1997**; http://shelx.uni-ac.gwdg.de/SHELX/index.html.
[17] *International Tables for X-ray Crystallography*, vol. 4, Kynoch Press, Birmingham, UK, **1974**.
[18] L. Zsolnai, G. Huttner, *XPMA*, University of Heidelberg, Heidelberg, **1994**; http://www.uni-heidelberg.de/institute/fak12/AC/huttner/software/software.html.
[19] R. Soltek, *Winray 32*, University of Heidelberg, **2000**; http://www.uni-heidelberg.de/institute/fak12/AC/huttner/software/software.html.
[20] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165–169; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* **1995**, *102*, 346–356; c) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119–124.
[21] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822–8824.
[22] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

Received: November 21, 2008
Published Online: March 31, 2009

