Zinc Amidinate Complexes

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Unexpected C–C Bond Formation and Synthesis of Tetranuclear Zinc Carbodiimide Clusters from the Reaction of $ZnMe_2$ and *i*PrN=C=N*i*Pr**

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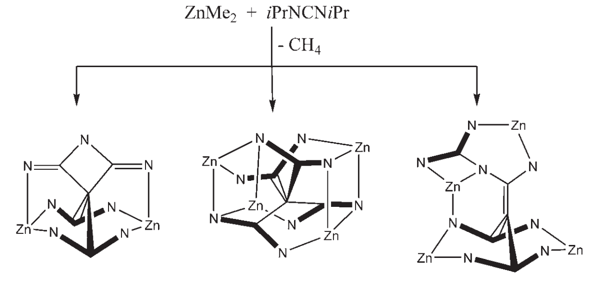
Dedicated to Professor Heinz-Dieter Fenske on the occasion of his 65th birthday

Anionic N,N-chelating ligands, such as β-diketiminate,[1] guanidinate,[2] and amidinate[3] ligands, have a long history in the synthesis of organometallic complexes of s-, p-, d-, and f-block metals,[4] most likely because their steric and electronic properties can easily be modified by simple variation of the substitution pattern. In addition, their capability to bind in both a bidentate (η^2) and a bridging monodentate (μ-η^1-η^1) fashion to the metal center, which allows the synthesis of tailor-made complexes with specific physical properties, makes them very useful in complex chemistry. The synthesis of zinc complexes of the desired type has mainly concentrated on β-diketiminato complexes of the type LZnR (L = β-diketiminate),[5] as these have been shown to be active catalysts in the ring-opening polymerization (ROP) of cyclic esters, in particular of lactides,[6] as well as in the copolymerization of CO_2 with various epoxides.[7] Furthermore, β-diketiminate substituents were shown to effectively stabilize unusual low-valent organozinc complexes.[8] In contrast, zinc amidinate und guanidinate complexes have been investigated to a far lesser extent. To the best of our knowledge, only a single benzamidinate and a very few mono or bis(guanidinate) zinc complexes,[9,10] which have also been investigated as ROP catalysts,[11] have been synthesized. In addition, mono and bis(anilido) complexes were obtained from the reaction of $ZnMe_2$ with *N*-2-pyridylaniline and some formamidinate and boraamidinate complexes have been structurally characterized.[12–14] Surprisingly, insertion reaction of carbodiimides $(RN)_2C$ with ZnR_2 have not been reported to date, even though this specific reaction type has been established in the past as a very powerful method for the synthesis of both main-group and transition-metal amidinate complexes.[15] Herein, we report on the synthesis and structure of polynuclear zinc amidinate complexes by reaction of $ZnMe_2$ with $(i\mathrm{PrN})_2C$.

Equimolar amounts of $ZnMe_2$ and $(i\mathrm{PrN})_2C$ dissolved in toluene react at 90 °C within 60 hours to give a mixture of several compounds, from which **1**, **2**, and **3** were isolated after workup by fractional crystallization from solutions in *n*-pentane at −30 °C (Scheme 1). In addition, **2** was obtained in higher yield after the reaction mixture was heated for five days at 100 °C.[16]



$[(\mathrm{MeZn})_2\{\mathrm{C}(i\mathrm{PrNCN}i\mathrm{Pr})_2\}\text{-}(i\mathrm{PrNCN}(i\mathrm{Pr})\mathrm{CN}i\mathrm{Pr})]$ **1**

$[(\mathrm{MeZn})_4\{\mathrm{C}(i\mathrm{PrNCN}i\mathrm{Pr})_4\}]$ **2**

$[(\mathrm{MeZn})_4\{\mathrm{C}(i\mathrm{PrNCN}i\mathrm{Pr})_4\}]$ **3**

Scheme 1. Synthesis of **1**, **2**, and **3**. Amidinate units containing a delocalized π-electron system are accentuated, Me and *i*Pr groups are omitted for clarity.

^{1}H and ^{13}C NMR spectra of **1**–**3** show the expected resonances of the organic substituents. Compound **2** shows a single resonance for the zinc methyl groups and two doublets and two septets for the nonequivalent *i*Pr groups, indicating that **2** adopts a symmetric structure in solution. In contrast, **3** shows four different resonances for the zinc methyl groups as well as eight resonances for the methine and sixteen for the methyl protons of the *i*Pr groups. ^{1}H NMR spectra of a reaction solution in [D$_8$]toluene, which was heated to 90 °C, were recorded over a period of six days to investigate the reaction mechanism in more detail. According to these studies, **3** is the first reaction product. Its intensity decreases after 36 hours with concomitant formation of **1** and **2**. The

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maximum concentration of **2** is reached after 72 hours, whereas **1** is the major product after 120 hours. A steadily increasing singlet at 0.20 ppm clearly indicates the formation of methane during the reaction,[17] which is most likely due to initial formation of $[\mathrm{MeZn}(i\mathrm{PrN})_2\mathrm{CMe}]$, which then consequently undergoes C–H activation of the methyl group of the amidinate unit and elimination of three equivalents of CH_4 with subsequent formation of **2** and **3**. Longer reaction times led to further decomposition reactions with formation of **1**, whereas no definite reaction product could be observed after 150 hours.

Single crystals of **1**, **2**, and **3** (Figures 1–3) were obtained from solutions in *n*-pentane.[18] All the compounds have a central carbon atom C_{center} (C7: **1**, C33: **2**, **3**), which is surrounded by sp^2-hybridized carbon atoms of neighboring amidinate moieties in a tetrahedral (**1**, **2**) or trigonal-planar (**3**) coordination mode, and an eight-membered $\{\mathrm{Zn}_2(\mu\text{-NCN})_2\}$ heterocycle containing two zinc atoms and two amidinate groups. The C–C_{center} bond lengths in **1** (1.524(2)–1.547(2) Å) and **2** (1.548(5)–1.566(5) Å) are in the typical range for C–C single bonds, whereas **3** contains two long (1.505(4), 1.506(4) Å) and one significantly shorter C–C bond (C19-C33 1.384(4) Å), which agrees with a C=C double bond. Atom C26 of the remaining fourth amidinate group **3** binds to N8 (1.493(4) Å) with subsequent formation of a guanidinate moiety. The N–C bond lengths observed for the amidinate groups in **1** (av. 1.333 Å), **2** (av. 1.334 Å), and **3** (av. 1.327 Å) clearly prove the formation of delocalized π-electron systems, except for the significantly elongated N8-C19/26 bond lengths in **3** (1.491(4)–1.502(4) Å), which can rather be described as classical single bonds. The N=C–N–C=N moiety in **1** has two short (N5–C5 1.268(2), N7–C6 1.266(2) Å) and two long N–C bond lengths (N6–C5 1.417(2), N6–C6 1.410(2) Å). The Zn–N bond lengths in **1** (2.108(2)–2.134(2) Å) and **2** (2.129(3)–2.172(3) Å) are almost identical, whereas **3** shows a much larger variation of almost 0.35 Å (Zn4–N5 1.957(2), Zn3–N8 2.319(2) Å). The Zn3–N8 bond is significantly elongated compared to the neighboring Zn3–N4/7 bonds (2.151(3), 1.979(3) Å).

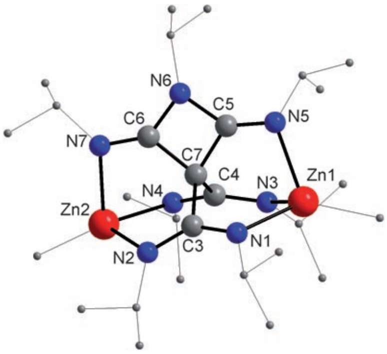

Figure 1. Molecular structure and atom numbering scheme of **1**. Hydrogen atoms are omitted for clarity; Me and *i*Pr groups are presented in a diminished fashion.

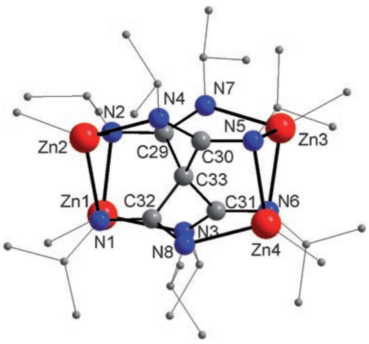

Figure 2. Molecular structure and atom numbering scheme of **2**. Hydrogen atoms are omitted for clarity; Me and *i*Pr groups are presented in a diminished fashion.

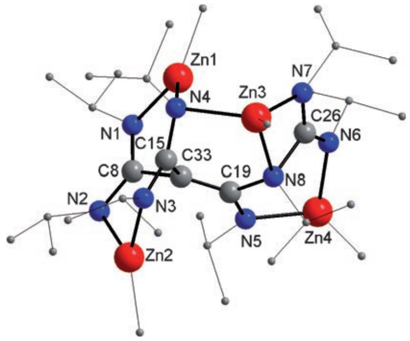

Figure 3. Molecular structure and atom numbering scheme of **3**. Hydrogen atoms are omitted for clarity; Me and *i*Pr groups are presented in a diminished fashion.

To better understand the bonding situation in **1**–**3**, DFT calculations with the corresponding *N*-methyl-substituted model compounds **1′**–**3′** were performed.[19] The Zn–N bonds show high ionic bonding contributions, and the C–C_{center} bonds are true single bonds, except for C33–C19 in **3**, which is more like a C=C double bond. The C–N bonds in the amidinato moieties in **1**–**3** are best described by two resonance structures ($N{=}C{-}N^{-}\leftrightarrow{}^{-}N{-}C{=}N$). The central framework of **1** is a four-membered ring with two additional amidinato substituents at the tetrahedrally coordinated C_{center} atom. The N=C–N–C=N subunit can be interpreted as a nitrogen analogue of a cyclic carboxylic acid anhydride. The shorter Zn–N bonds observed for the "amidinato" nitrogen atom compared to the "anhydride" nitrogen atoms in **1** correlate with the different partial atomic charges,[20] which are more negative at the formally half-negatively charged "amidinato" nitrogen atoms compared to the formally neutral "anhydride" nitrogen atoms. The framework of **2** is best described as tetrakis(amidinato)methane. The asymmetry of the amidinate moieties correlates with the different partial atomic charges of the nitrogen atoms, which increases with increasing number of bonded zinc atoms. Consequently, those nitrogen atoms bonded to two zinc atoms have higher charge densities and thus slightly elongated C–N bond lengths, that is, the two boundary structures are weighted differently. Atoms C33, C19, and N5 in **3** build a central enamide moiety, which can be described by two mesomeric structures ($C{=}C{-}N^{-}\leftrightarrow{}^{-}C{-}C{=}N$). C33 binds to two additional amidinate groups, which are part of an eight-membered $\{\mathrm{Zn}_2(\mu\text{-NCN})_2\}$ ring, whereas C19 is connected by N8 to the additional guanidinate unit. The N8–C19 and N8–C26 bonds are typical single bonds without any π-bonding contribution. The lowest atomic charge of all nitrogen atoms was found for N8 in **3**, which agrees very well with the very long Zn3–N8 bond length.

Compounds **2** and **3** are constitutional isomers. The transformation of **3** into **2** requires breakage of the N8–C26 bond and formation of the C26–C33 bond, adjustment of the π-bonding electrons of the C19–C33 bond into the amidinate unit (N5–C19–N8), and formation of three additional Zn–N bonds. According to the theoretical calculations, **3′** is about 16.6 kcal mol^{-1} higher in energy than **2′**. This agrees very well with the experimental observations that **3** is a reaction intermediate on the way to the formation of **2**.

The unexpected synthesis of **1**–**3** raises the question as to whether other organometallic compounds also initiate such C–C bond formation reactions. To date, there are no references in the literature. In addition, the potential application of **1**–**3** to serve as single molecule precursors for the synthesis of zinc carbonitride as well as their use as polymerization catalyst are currently being investigated.

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[18] Details of the X-ray structural analysis and selected bond lengths and angles are given in the Supporting Information. CCDC-661399 (**1**), CCDC-661400 (**2**), and CCDC-661401 (**3**) 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.

[19] DFT calculations of **1′**–**3′** were performed with the Gaussian03 program package (M. J. Frisch, et al. Gaussian 03, Revision D.02; Gaussian Inc., Pittsburgh, PA, **2003**, complete reference is given in the Supporting Information). The energies of the molecular structures were optimized at B3LYP/SVP level; SVP is the split-valence basis set with additional polarizations functions from: A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571; A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829.

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