

Zinc Carbodiimide Cluster Complexes: Synthesis, X-ray Crystal Structures, and Reaction Mechanism

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Reactions of Me_2Zn with carbodiimides $C(NR)_2$ in different molar ratios at elevated temperature were investigated, a possible reaction mechanism was identified, and the single-crystal X-ray structures of polynuclear amidinate zinc complexes { $C[C(NCy)_2ZnMe]_4$ }, 1, { $C[C(NCy)_2ZnMe]_3$ -(ZnMe)}, 3, and { $C[C(NCy)_2ZnMe]_3$ (ZnMe)(MeZnOMe)}, 5, are reported.

Introduction

Guanidinate¹ and amidinate anions² have a long tradition in coordination chemistry of s-, p-, d-, and f-block metals.³ They can bind to the metal center as monodentate (η^1, \mathbf{a}) , chelating (η^2, \mathbf{b}) , or bridging monodentate $(\mu - \eta^1 - \eta^1, \mathbf{c})$ four-electron donor ligands,⁴ and their steric and electronic properties can easily be tuned by variation of the organic substituents R and R', rendering them very suitable for the synthesis of *tailor-made* complexes. These complexes, which show promising applications in catalysis,⁵ material sciences (i.e., precursors for CVD),⁶ and the synthesis of organic–inorganic hybrid materials, are typically prepared by salt elimination reaction or carbodiimide insertion reaction into metal–C and metal–N bonds.⁷

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Scheme 1. Salt Elimination Reaction and Carbodiimide Insertion Reaction

L _x MCI + Li[RC(NR') ₂]	-LiCl	L _x M[(R'N) ₂ CR]
L _x MR + C(NR') ₂	>	L _x M[(R'N) ₂ CR]

Considering the general interest in metal amidinate complexes, it came to us as a surprise that zinc amidinate complexes were almost unknown,⁸ whereas the corresponding guanidinate complexes, which are of potential interest in ROP catalysis, have been studied in more detail.⁹ Therefore, we became interested in this specific class of compounds and reported very recently on the synthesis of several mono- and bisamidinate complexes of the type LZnX and L₂Zn (L = amidinate) by salt elimination reaction.¹⁰ Moreover, reactions of carbodiimides C(NR)₂ with ZnR₂ were shown to proceed either with insertion of the carbodiimide into the Zn-C bond and subsequent formation of the expected amidinate complex such as [EtC(N*i*-Pr)₂ZnEt]₂ or with unexpected formation of cluster-type complexes such as {C-[C(N*i*-Pr)₂ZnMe]₄}.¹¹

To the best of our knowledge, the latter reaction, which proceeds with C–C bond formation, is without precedent in carbodiimide chemistry. Therefore, we studied reactions of ZnMe₂ with different carbodiimides in more detail in order to clarify if this is a general reaction pathway for organozinc reagents and to identify a possible reaction mechanism. Herein, we report on the synthesis and characterization of four amidinate zinc complexes: {C[C(NCy)₂ZnMe]₄}, **1**, {C[C(NCy)₂ZnMe]₂[C₂(NCy)₃]}, **2**, {C[C(NCy)₂ZnMe]₃-(ZnMe)}, **3**, and {C[C(NCy)₂ZnMe]₃(NCy₂ZnMe)}, **4**. In addition, the partially oxidized complex {C[C(NCy)₂ZnMe]₃(znMe)], **5**, was characterized by single-crystal X-ray diffraction.

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Figure 1. Solid-state structure of **1** (stick-and-ball model). H atoms are omitted for clarity; Me and Cy groups are presented in a diminished fashion. Selected bond lengths [Å] and angles [deg]: Zn1–N1 2.151(3), Zn1–N2 2.145(3), Zn1–N4 2.172(3), N1–C28 1.311(5), N2–C28a 1.350(5), N3–C27a 1.318(5), N4–C27 1.346(5), C27–C29 1.564(5), C28–C29 1.564(5); N1–Zn1–N2 93.73(12), N2–Zn1–N4 83.27(12), N1–Zn1–N4 97.24(12), N3a–C27–N4 137.3(3), N1–C28–N2a 137.4(4), C27–C29–C28 101.06(18), C27a–C29–C28 130.78(19), C28a–C29–C28 98.7(4).

Scheme 2. Complexes Resulting from Insertion Reactions of C(Ni-Pr)₂ with ZnMe₂ and ZnEt₂



Results and Discussion

Solutions of equimolar amounts of $ZnMe_2$ and $C(NR)_2(R = t-Bu, SiMe_3, Cy, Dipp)$ in toluene were stirred at 110 °C for 60 h. No reaction was observed for the sterically hindered carbodiimides (R = t-Bu, SiMe_3, Dipp),¹² whereas reactions with cyclohexyl carbodiimide $C(NCy)_2$ produced more or less complex reaction mixtures of complexes 1–4.

A rather strong influence of several specific reaction parameters such as molar ratio, reaction temperature (90, 110 °C), and reaction time (3-5 days) on the formation of the preferred reaction product(s) 1-4 was observed. Moreover,



Figure 2. Solid-state structure of complex **2** illustrating the connectivity within this complex. H atoms are omitted for clarity; Me and Cy groups are presented in a diminished fashion.



Figure 3. Solid-state structure of **3** (stick-and-ball model). H atoms are omitted for clarity; Me and Cy groups are presented in a diminished fashion. Selected bond lengths [Å] and angles [deg]: Zn1–N1 2.051(3), Zn1–N2 1.990(3), Zn2–N1 2.059(3), Zn2–N3 1.968(3), N1–C7 1.429(5), N2–C7 1.331(5), N3–C9 1.342(4), C7–C8 1.425(4), C8–C9 1.499(7); N1–Zn1–N2 66.58(12), N1–Zn2–N3 92.36(12), N1–C7–N2 106.9(3), N3–C7–C8 122.3(3), C7–C8–C7a 123.7(5), C7–C8–C9 118.1(2).

the use of carefully purified cyclohexyl carbodiimide turned out to be essential; otherwise the partially oxidized complex $\{C[C(NCy)_2ZnMe]_3(ZnMe)(MeZnOMe)\}, 5$, was formed to some extent.¹³

¹H NMR spectra of the bulk reaction products typically showed multiple resonances due to the presence of nonequivalent Zn-Me and Cy groups.¹⁴ Complexes {C[C(NCy)₂Zn-Me]₄}, **1**, {C[C(NCy)₂]₂Zn₂Me₂[C₂(NCy)₃]}, **2**, {C[C(NCy)₂-ZnMe]₃(ZnMe)}, **3**, and {C[C(NCy)₂ZnMe]₃(NCy₂ZnMe)}, **4**,

⁽¹²⁾ More drastic reaction conditions (no solvent, T = 140 °C) results in decomposition of ZnMe₂ with subsequent formation of elemental zinc.

⁽¹³⁾ The reaction of ZnMe₂ with unpurified C(NCy)₂ was repeated several times, in all cases yielding mixtures of 1-5 with up to 5% 5. Single crystals of 5 (mixture together with 2) were isolated from different reaction batches after fractional crystallization from solutions in *n*pentane at -30 °C and identified by single-crystal X-ray diffraction.

⁽¹⁴⁾ The methine H atom (C1H) is the only resonance of the Cy group that clearly indicates the formation of multiple species since the resonances of other H atoms of this group (C2H-C6H) are rather broad and overlap.



 N6
 N4

 C3
 C4
 C2

 N2
 N1
 N1

 N5
 C1
 Zn5

 Zn3
 Zn1
 Zn2

Figure 4. Solid-state structure of 5 (stick-and-ball model). H atoms are omitted for clarity; Me and Cy groups are presented in a diminished fashion. Selected bond lengths [Å] and angles [deg]: Zn1–O1 2.015(2), Zn1–N3 2.269(2), Zn1–N5 2.249(2), Zn2–N1 2.121(2), Zn2–N3 2.148(2), Zn3–N2 2.098(2), Zn3–N5 2.187(2), Zn4–N4 2.027(2), Zn4–N6 2.031(2), Zn5–N1 2.027(2), Zn5–N2 2.043(2), N1–C1 1.416(3), N2–C1 1.422(3), N3–C2 1.369(3), N4–C2 1.310(3), N5–C3 1.366(3), N6–C3 1.317(3), C1–C4 1.358(4), C2–C4 1.507(3), C3–C4 1.509(3); N1–Zn2–N3 92.77(8), N2–Zn3–N5 92.32(8), N4–Zn4–N6 95.78(9), N1–Zn5–N2 69.02(9), N1–C1–N2 108.7(2), N3–C2–N4 135.4(2), N5–C3–N6 135.1(2), C1–C4–C2 121.8(2), C1–C4–C3 122.0(2), C2–C4–C3 113.8(2).

were isolated from these reaction mixtures by fractional crystallization from solutions in cyclohexane (1, 3, 4) at +4 °C or pentane/toluene (2) at -30 °C. ¹H and ¹³C NMR spectra of pure 1-4 show the expected resonances of the organic substituents. Only a single resonance for the Zn-Me group is observed for 1-3, indicating these complexes adopt symmetric structures in solution. In contrast, complex 4 shows four Zn-Me resonances, as was observed for the corresponding i-Pr-substituted complex.¹¹ The Cy groups of 1-4 show more complex patterns, including two (1) and three (2) resonances of the C1Hax protons with expected 1:1 (1) and 4:2:1 (2) molar ratios. 3 shows only a single C1H_{ax} resonance, whereas four well-separated C1H_{ax} resonances with equal intensity and one broad resonance with a 4-fold intensity due to an overlap of four Cy groups are observed for 4. ¹H NMR spectra of 1-4 recorded at 300 MHz show rather broad signals, as was previously observed for monoamidinate zinc halides [t-BuC(NCy)2]ZnX



Figure 5. Central cluster cores of 5 and 6 demonstrating the structural relationship between both clusters. Substituents bound to the N atoms have been omitted for clarity.

Table 1. Influence of Specific Reaction Parameters on the For-
mation of Complexes $1-4^a$

:	molar ra	tio (ZnMe	₂ /C(NCy) ₂); reactio	n temper	ature [°C]
	1:2		1:1		2:1	
reaction time [d]	90 °C	110 °C	90 °C	110 °C	90 °C	110 °C
3 4 5	2	2	4	1	3 + 4	3

 $^{a}\{C[C(NCy)_{2}ZnMe]_{4}\}, 1, \{C[C(NCy)_{2}]_{2}Zn_{2}Me_{2}[C_{2}(NCy)_{3}]\}, 2, \{C[-C(NCy)_{2}ZnMe]_{3}(ZnMe)\}, 3, \{C[C(NCy)_{2}ZnMe]_{3}(NCy_{2}ZnMe)\}, 4.$

(X = Cl, Br), whereas spectra recorded at 500 MHz show well-resolved resonances of the axial H atoms (H_{ax}) with large coupling constants to the axial (dihedral angle around 180°) and small coupling constants to the equatorial H atoms (dihedral angle around 60°) of adjacent CH₂ groups. For instance, the H1_{ax} protons (triplet of triplet) and the H4_{ax} protons (triplet of quartet) of 1-4 show significantly larger coupling constants to the axial H atoms $({}^{3}J_{H_{ax}H_{ax}} = 10-13 \text{ Hz})$ than to the equatorial ones (${}^{3}J_{H_{ax}H_{eq}} = 3-4$ Hz). In contrast, the equatorial H atoms show only broad doublets due to large geminal ${}^{2}J_{\rm HH}$ couplings, with the broadening resulting from small ${}^{3}J_{\rm HH}$ couplings to the magnetically nonequivalent axial and equatorial H atoms of the adjacent CH₂ groups (spectrum of higher order). Comparable findings were previously observed for the bisamidinate complex [t-BuC(NCy)₂]₂Zn, in which the ¹H resonances were assigned by HH-COSY and

Scheme 4. Possible Mechanism of a Stepwise Deprotonation/ Carbodiimide Insertion Reaction



DPFGSE-NOE spectroscopy studies.¹⁰ **5** was formed as a byproduct in low yields only when the carbodiimide was used as received.¹⁵ The most prominent resonances for **5** are sharp singlets at 3.58 and -0.37 ppm due to the presence of the MeZnOMe moiety. Single crystals of **5** were isolated manually from a mixture of **2** and **5** after recrystallization from a solution in *n*-pentane at -30 °C.

Single crystals of 1, 2, 3, and 5 were obtained from solutions in cyclohexane (1, 3), *n*-pentane/toluene (2), and *n*-pentane (5), respectively. Unfortunately, the quality of the crystals of 2 was too low to allow a reasonable refinement of the data, but the connectivity of the atoms within 2 was proven without any doubts. Moreover, the structures of 1 and 2 are comparable to those observed for the *i*-Pr-substituted complexes,^{11b} clearly demonstrating that the formation of such polynuclear clusters is a general reaction pathway in ZnMe₂/carbodiimide chemistry. Both complexes contain a central C atom (C29 1, C50 2), which is tetrahedrally coordinated by four C atoms of adjacent amidinate groups. The equal C–C bond lengths in 1 (1.564(2) Å) clearly prove the formation of C-C single bonds. The almost equal Zn-N bond lengths in 1 (2.141(3)-2.180(3) Å) are slightly elongated compared to the *i*-Pr-substituted derivative (2.108(2)-2.134(2) Å), whereas the Zn-C bond lengths of 1 (1.979(4), 1.983(4) Å) are slightly shorter. The N-C bond lengths within the amidinate groups in 1 indicate a delocalized π -electron system, even though the N-C bond lengths of the 3-foldcoordinated N atoms (N1-C28 1.311(5), N3-C27A 1.318(5) Å) are slightly shorter compared to those of the 4-fold-coordinated N atoms (N2-C28A 1.350(5), N4-C27 1.346(5) Å), as was expected.

The structures of **3** and **5** are more complex compared to **1** and **2**. Both complexes exhibit a central cluster core built by three amidinate and four ZnMe groups, and the C atoms of the amidinate groups (C7, C9, C7a **3**; C1, C2, C3 **5**) bind to a central, trigonal-planar coordinated carbon atom (C8 **3**; C4 **5**). However, the bonding situation in **3** and **5** clearly differs. In **3**, one amidinate group serves as bridging and two as chelating ligand, whereas in **5**, the amidinate groups serve as

bridging bidentate ligands, resulting in the formation of a 12-membered $Zn_3(\mu$ -NCN)₃ ring. In addition, one of the three amidinate moieties (N1-C1-N2) in 5 binds to a fourth Zn atom (Zn5) in a N,N'-chelating mode. Even more remarkable are the different bonding situations within the central CC₃ moieties. **3** shows two short (C8–C7 1.425(4) Å) and one long C-C bond (C8-C9 1.499(7) Å), whereas in 5, two long (C2-C4 1.507(3), C3-C4 1.509(3) Å) and one short C-C bond (C1-C4 1.358(4) Å) rather point to the formation of two C-C single and one C=C double bond. The π -electron systems of two amidinate groups in 3 (N1– C1-N2) and 5 (N3-C2-N4, N5-C3-N6) are significantly disturbed and show different C-N bond lengths (1.331(5), 1.429(5) Å 3; 1.310(3)-1.369(3) Å 5), most likely caused by the different coordination numbers of the N atoms (three vs four). In contrast, the N-C bond lengths within the N3–C9–N3a unit in 3 indicate a delocalized π -electron system (1.342(4) Å), whereas those of the N1-C1-N2 moiety in 5 rather point to N-C single-bond character (1.416(3), 1.422(3) A).

The formation of the new cluster-type complexes 1-5 can be rationalized by a stepwise metalation reaction of the zinc amidinate complex [MeC(NCy)₂]ZnMe, **A**, which is most likely initially formed in the reaction, followed by insertion of the carbodiimide into the as-formed Zn–C bond with subsequent formation of complexes **B** and **C**.¹⁶

Complexes A, B, and C may also adopt heterocyclic structures with bridging amidinate groups rather than with N,N'-chelating groups, as was observed for $\{[t-BuC(Ni-Pr)_2]-ZnMe\}_2$.¹⁷ Moreover, C can undergo a *keto-enol* transformation with subsequent formation of C'. As a consequence, deprotonation reaction with ZnMe_2 can occur at either the carbon or the nitrogen atom, yielding two different reaction products, **D** and **D**'.

D reacts with $C(NCy)_2$ with insertion into the Zn-C bond and subsequent formation of E, which after rearrangement of the amidinate groups from a chelating to a bridging binding mode yields 1, whereas the reaction of D', which represents exactly the cluster core as observed in 5 (5 contains only an additionally coordinated MeZnOMe molecule), with $C(NCy)_2$ occurs with insertion into the Zn-N bond (Zn5-N1) and formation of \mathbf{E}' , containing a guanidinate group, as was previously observed in $\{(MeZn)_4C[(i-PrNCNi-Pr)_4]\}$, 6^{11b} In 6 the carbodiimide insertion occurred into the Zn4–N8 bond, yielding the guanidinate moiety N6–C26 (N7)-N8. Chang et al. and Barry et al. previously reported that sterically less hindered carbodiimides prefer insertion reaction into an Al-N bond, whereas sterically more hindered carbodiimides insert into the Al-Me bond of Me₂AlNMe₂.¹⁸

As a consequence of this insertion reaction, an NCNCN unit is formed as is observed in $\{C[C(NCy)_2]_2Zn_2Me_2-[C_2(NCy)_3]\}$, **2**, as well as in the *i*-Pr-substituted complex

⁽¹⁵⁾ Even though 1-4 as well as $ZnMe_2$ are sensitive to oxygen, the formation of 5 due to the presence of adventitious oxygen in the system can be excluded. According to ¹H NMR spectroscopic studies, 5 was only formed in three different reactions when the carbodiimide was used as received. In contrast, no indication for the formation of 5 was found in reactions with purified carbodiimide.

⁽¹⁶⁾ Since $ZnMe_2$ is a rather poor base, it is not quite clear why the deprotonation reaction occurs in these reactions. Moreover, we have not found any indication for a deprotonation mechanism in reactions of carbodiimides with AlMe₃ and GaMe₃, respectively, even at elevated temperatures. Currently we are investigating reactions of monoamidinate zinc complexes of the type $[MeC(NR)_2]ZnMe$ with strong bases such as organolithium compounds.

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Scheme 6. Possible Reaction Mechanism for the Formation of 3 and 5



 $\{C[C(N$ *i* $-Pr)_2]_2Zn_2Me_2[C_2(N$ *i* $-Pr)_3]\}, 7.$ Formally, **2** and **7** are formed by elimination of one molecule of RN(ZnMe)_2.

The formation of complexes 3 and 5 starting from D' can also be explained by rearrangement of the amidinate units from a chelating into a bridging binding mode. 3 is formed by rearrangement of two amidinate units, whereas 5 results from a rearrangement of three amidinate units, as shown in Scheme 6.

Conclusions

Cluster-type zinc amidinate complexes 1-5 were synthesized by reaction of $ZnMe_2$ and cyclohexyl carbodiimide and structurally characterized. A possible reaction mechanism, which explains the formation of the complexes 1-5 as well as those reported previously, has been identified. Further studies on the reaction of $ZnMe_2$ with carbodiimides and other heterocumulenes are currently under investigation.

Experimental Details

All manipulations were performed under an Ar atmosphere. Solvents were carefully dried over Na/K and degassed prior to use. Cyclohexyl carbodiimide was heated to 40 °C and evacuated for 6 h at 10^{-3} mbar. A 1.2 M solution of ZnMe₂ in toluene was purchased from Acros and used as received. ¹H and ¹³C{¹H} NMR spectra were recorded on Bruker DMX 300 or Bruker Avance 500 spectrometers and are referenced to internal C₆D₅H (¹H: $\delta = 7.154$; ¹³C: $\delta = 128.0$). IR spectra were recorded on an ALPHA-T FT-IR spectrometer either in Nujol between KBr plates or with a single-reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Essen.

{C[C(NCy)₂ZnMe]₄}, 1. ZnMe₂ (4.2 mL, 1.2 M in toluene, 5 mmol) and 1.03 g (5 mmol) of purified (CyN)₂C were stirred for 5 days at 110 °C. All volatiles were removed at reduced pressure, and the resulting solid was dissolved in 30 mL of cyclohexane and stored at +4 °C. Colorless crystals of 1 were formed within 24 h and isolated by filtration.

Yield (isolated crystals): 0.84 g (58%). Melting point: > 210 °C. Anal. Found (calcd) for $C_{57}H_{100}N_8Zn_4$ (1158.95 g/mol): H, 8.72 (8.70); C, 59.19 (59.07); N, 9.62 (9.67). ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ 0.14 (s, 3H, Zn*Me*), 1.19–1.24 (m, 6H, *CH*₂), 1.51–1.54 (m, 2H, *CH*₂), 1.69 (m (br), 2H, *CH*₂), 1.85 (m (br), 8H, *CH*₂), 2.36–2.40 (m, 2H, *CH*₂), 3.68 (tt, ³J_{Harma}=10.6 Hz, 1H, H(1)_{ax}), 4.01 (m, 1H, H(1)_{ax}). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ 1.0 (s, Zn*Me*), 26.1 (s, C3/C5), 27.2 (s, C4), 34.7 (C2/C6), 34.8 (C2/C6), 56.4 (s, N-C1), 58.6 (s, N-C1), 170.6 (s, NCN). IR: ν 2924, 2849, 2657, 1688, 1550, 1510, 1449, 1379, 1342, 1279, 1259, 1086, 1014, 957, 930, 891, 863, 795, 702, 678, 659, 515 cm⁻¹.

{C[C(NCy)₂ZnMe]₂[C₂(NCy)₃]}, 2. ZnMe₂ (4.2 mL, 1.2 M in toluene, 5 mmol) and 2.06 g (10 mmol) of purified (CyN)₂C were stirred for 5 days at 110 °C. All volatiles were removed at reduced pressure, and the resulting solid was dissolved in 30 mL of cyclohexane and stored at +4 °C.

Colorless crystals of **2** were formed within 24 h and isolated by filtration.

Yield (isolated crystals): 0.61 g (27%). Melting point: 118 °C. Anal. Found (calcd) for $C_{49}H_{83}N_7Zn_2$ (900.98 g/mol): H, 9.18 (9.28); C, 65.24 (65.32); N, 10.85 (10.88). ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ 0.13 (s, 6H, Zn*Me*), 0.79 (m, 3H, CH₂), 1.05–1.21 (m, 7H, CH₂), 1.34 (m (br), 16H, CH₂), 1.48–1.74 (m, 12H, CH₂), 1.80–2.05 (m (br), 28H, CH₂), 2.18–2.21 (m, 4H, CH₂), 3.43 (tt, ³J_{HaxHax} = 11.3 Hz, 1H, H(1)_{ax}), 3.54 (tt, ³J_{HaxHax} = 10.8 Hz, ³J_{HaxHax} = 3.8 Hz, 2H, H(1)_{ax}), 3.96 (tt, ³J_{HaxHax} = 10.3 Hz, 4H, H(1)_{ax}). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ – 3.9 (s, Zn*Me*), 25.5 (s, Cy), 26.1 (s, Cy), 26.4 (s, Cy), 26.5 (s, Cy), 26.6 (s, Cy), 27.2 (s, Cy), 29.6 (s, Cy), 31.5 (s, CC4), 34.2 (s, C2/C6), 36.0 (s, C2/C6), 36.5 (s, C2/C6), 57.0 (N-C1), 58.8 (N-C1), 155.5 (s, NCN), 160.0 (s, NCN). IR (Nujol): *v* 2924, 2854, 1686, 1556, 1462, 1377, 1344, 1312, 1286, 1260, 1090, 1021, 889, 799, 722, 652, 512 cm⁻¹.

{C[C(NCy)₂ZnMe]₃(ZnMe)}, 3. ZnMe₂ (8.4 mL, 1.2 M in toluene, 10 mmol) and 1.03 g (5 mmol) of purified (CyN)₂C were stirred for 5 days at 110 °C. All volatiles were removed at reduced pressure, and the resulting solid was dissolved in 30 mL of cyclohexane and stored at +4 °C. Colorless crystals of **2** were formed within 24 h and isolated by filtration.

Yield (isolated crystals): 0.58 g (49%). Melting point: 140 °C. Anal. Found (calcd) for $C_{44}H_{78}N_6Zn_4$ (952.62 g/mol): H, 8.19 (8.25); C, 55.33 (55.48); N, 8.74 (8.82). ¹H NMR (500 MHz, C_6D_6 , 25 °C): δ 0.03 8s, 3H, Zn*Me*), 1.02–1.11 (tt, 1H, ${}^3J_{H_{ar}H_{ar}}$ = 13.1 Hz, ${}^3J_{H_{ar}H_{ar}}$ = 3.7 Hz, H(4)_{ax}), 1.19–1.28 (m, 4H, H(3/5)_{ax}), 1.38–1.45 (m, 4H, H(2/6)_{ax}), 1.51 (d (br), 2H, H(4)_{eq}), 1.69 (d (br), 4H, H(3/5)_{eq}), 2.10 (d (br), 4H, H(2/6)_{eq}), 3.56 (tt, ${}^3J_{H_{ar}H_{ar}}$ = 3.5 Hz, 2H, H(1)_{ax}). ¹³C NMR (125 MHz, C_6D_6 , 25 °C): δ 1.4 (s, Zn*Me*), 24.9 (s, Cy), 25.6 (s, Cy), 25.8 (s, Cy), 25.9 (s, Cy), 26.1 (s, Cy), 26.5 (s, Cy), 26.8 (s, Cy), 27.2 (s, Cy), 35.4 (s, Cy), 39.0 (s, Cy), 37.3 (s, Cy), 37.5 (s, Cy), 57.3 (s, Cy), 57.5 (s, Cy), 61.0 (s, Cy), 174.4 (s, NCN). IR (Nujol): ν 2924, 2853, 1644, 1529, 1506, 1461, 1406, 1377, 1341, 1309, 1262, 1242, 1194, 1177, 1088, 1072, 1026, 976, 890, 841, 803, 723, 862, 652, 603, 564, 548 cm⁻¹.

{C[C(NCy)₂ZnMe]₃(NCy₂ZnMe)}, 4. ZnMe₂ (4.2 mL, 1.2 M in toluene, 5 mmol) and 1.03 g (5 mmol) of purified (CyN)₂C were stirred for 4 days at 90 °C. All volatiles were removed at reduced pressure, and the resulting solid was dissolved in 30 mL of cyclohexane and stored at +4 °C. Colorless crystals of 4 were formed within 24 h and isolated by filtration.

Yield (isolated crystals): 1.45 g (78%). Melting point: 150 °C. Anal. Found (calcd) for C₅₇H₁₀₀N₈Zn₄ (1158.95 g/mol): H, 9.33 (8.70); C, 61.18 (59.07); N, 8.94 (9.67). ¹H NMR (500 MHz, C_6D_6 , 25 °C): $\delta - 0.08$ (s, 3H, ZnMe), -0.06 (s, 2H, ZnMe), -0.06 (0.02 (s, 3H, ZnMe), 0.08 (s, 3H, ZnMe), 1.01-1.15 (m, 6H, CH₂), 1.16-1.37 (m, 20H, CH₂), 1.42-1.45 (m, 2H, CH₂), 1.46-1.55 (m, 14H, CH₂), 1.56-1.67 (m, 8H, CH₂), 1.67-1.78 (m, 12H, CH_2), 1.79–1.95 (m, 6H, CH_2), 2.03–2.20 (m, 6H, CH₂), 2.22-2.28 (m, 2H, CH₂), 2.29-2.38 (m, 4H, CH₂), 2.39-CH₂), 2.22–2.28 (m, 2H, CH₂), 2.29–2.36 (m, 4H, CH₂), 2.39– 2.51 (m, 2H, CH₂), 3.16 (tt, ${}^{3}J_{H_{ax}H_{ax}} = 10.7$ Hz, ${}^{3}J_{H_{ax}H_{eq}} = 3.4$ Hz, 1H, H(1)_{ax}), 3.70 (tt, 1H, H(1)_{ax}), 3.71 (tt, 1H, H(1)_{ax}), 3.77 (1H, H(1)_{ax}), 3.83 (tt, ${}^{3}J_{H_{ax}H_{ax}} = 10.9$ Hz, ${}^{3}J_{H_{ax}H_{eq}} = 3.8$ Hz, 1H, H(1)_{ax}), 4.00 (1H, H(1)_{ax}), 4.22 (tt, ${}^{3}J_{H_{ax}H_{ax}} = 10.7$ Hz, ${}^{3}J_{H_{ax}H_{eq}} = 3.6$ Hz, 1H, H(1)_{ax}), 4.40 (tt, ${}^{3}J_{H_{ax}H_{ax}} = 10.6$ Hz, ${}^{3}J_{H_{ax}H_{eq}} = 3.9$ Hz, 1H, H(1)_{ax}). ${}^{13}C$ NMR (125 MHz, C₆D₆, 25 °C): ${}^{\circ}C_{10}M_{e}$) = 7.2 (s, ${}^{\circ}T_{0}M_{e}$) = 7.2 (s, ${}^{\circ}T_{0}M_{e})$ = 7 ZnMe), -10.2 (s, ZnMe), -7.9 (s, ZnMe), -7.2 (s, ZnMe), 25.4 (Cy), 25.6 (Cy), 25.8 (Cy), 25.9 (Cy), 26.0 (Cy), 26.0 (Cy), 26.0 (Cy), 26.0 (Cy), 26.1 (Cy), 26.2 (Cy), 26.2 (Cy), 26.3 (Cy), 26.3 (Cy), 26.4 (Cy), 26.7 (Cy), 27.2 (Cy), 30.2 (s, Cy), 31.4 (s, Cy), 32.3 (s, Cy), 33.2 (s, Cy), 35.7 (s, Cy), 36.0 (s, Cy), 36.3 (s, Cy), 36.3 (s, Cy), 36.4 (s, Cy), 36.8 (s, Cy), 36.9 (s, Cy), 37.4 (s, Cy), 37.6 (s, Cy), 37.8 (s, Cy), 37.8 (s, Cy), 38.2 (s, Cy), 38.5 (s, Cy), 56.1 (s, Cy), 56.2 (s, Cy), 56.3 (s, Cy), 56.7 (s, Cy), 56.9 (s, Cy), 57.3 (s, Cy), 58.3 (s, Cy), 64.4 (s, Cy), 152.5 (s, NCN), 159.5

(s, NCN), 165.2 (s, NCN), 170.1 (s, NCN). IR (Nujol): ν 2924, 2853, 1573, 1534, 1462, 1377, 1341, 1302, 1276, 1260, 1166, 1153, 1128, 1086, 1057, 1043, 1023, 974, 955, 890, 840, 799, 722, 705, 676, 661, 646, 561, 545, 529 cm⁻¹.

{C[C(NCy)₂ZnMe]₃(ZnMe)(MeZnOMe)}, **5**, was obtained as a byproduct only when the carbodiimide was used as received. Unfortunately, we were not able to isolate a larger amount of **5**, but its formation is indicated by sharp singlets at 3.58 and -0.37 ppm due to the MeZnOMe moiety in the ¹H NMR spectra of the raw products of several reaction batches. According to these NMR spectra, **5** is formed in less than 5% vield.

Single-Crystal X-ray Analyses. Data were collected on a Bruker AXS SMART APEX CCD diffractometer (Mo K α radiation, $\lambda = v 0.71073$ Å; T = 173(2) K). The structures were solved by direct methods (SHELXS-97)¹⁹ and refined by full-matrix least-squares on F^2 . Semiempirical absorption corrections were applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms by a riding model (SHELXL-97, Program for Crystal Structure Refinement).²⁰

1: $C_{57}H_{100}N_8Zn_4 \cdot 2.5C_6H_{12} \cdot 1.5C_6H_6$, M = 1486.48, colorless crystal ($0.26 \times 0.18 \times 0.13$ mm); monoclinic, space group C2/c; a = 27.9483(7) Å, b = 15.6718(4) Å, c = 26.9271(10) Å; $\beta = 115.2140(10)^\circ$, $V = v \ 10670.4(6)$ Å³; Z = 4; $\mu \ v = 0.923$ mm⁻¹; $\rho_{\text{ber.}} = 0.925$ g cm⁻³; 63.763 reflections ($2\theta_{\text{max}} = 56.6^\circ$), 13.204 unique ($R_{int} = 0.0581$); 529 parameters; largest max./min. in the final difference Fourier synthesis 0.769 e $Å^{-3}/-0.584$ e $Å^{-3}$; max./min. transmission 0.75/0.64; $R_1 = 0.0738 (I > 2\sigma(I)), wR_2$ (all data) = 0.2344. The cyclohexane and benzene molecules refined with reduced SOF 0.5 together with the riding hydrogen atoms. In spite of the reduced SOFs of the solvent molecules, the ADPs still indicate severe disorder, which could not be resolved. 3: $C_{44}H_{78}N_6Zn_4 \cdot 2C_5H_{12}$, M = 1120.92, colorless crystal $(0.26 \times 0.18 \times 0.15 \text{ mm})$; monoclinic, space group P2/c; a =10.4638(7) Å, b = 14.5915(9) Å, c = 19.999(12) Å; $\beta = 95.887(4)^{\circ}$, V = 3037.5(3) Å³; Z = 2; $\mu = 1.598$ mm⁻¹; $\rho_{\text{ber.}} = 1.226$ g cm⁻³; 44 047 reflections ($2\theta_{\text{max}} = 49.6^{\circ}$), 5212 unique ($R_{\text{int}} = 0.0769$); 293 parameters; largest max./min. in the final difference Fourier synthesis 0.524 e $Å^{-3}$ /-0.329 e $Å^{-3}$; max./min. transmission 0.75/0.53; $R_1 = 0.0425 (I > 2\sigma(I))$, wR_2 (all data) = 0.1122. The elemental cell contains two cyclohexane C(31)-C(36) and C(41)-C(46), which are disordered over two sites with SOF 0.5 together with the riding hydrogen atoms and refined with isotropic displacement parameters. 5: C46H84N6OZn5.1.25 C_5H_{12} , M =1161.26, colorless crystal (0.32 × 0.26 × 0.22 mm); triclinic, space group $P\overline{1}$; a = 12.8446(9) Å, b = 13.7719(10)Å, c =19.7904(13) Å; $\alpha = 94.978(4)^{\circ}$, $\beta = 108.659(3)^{\circ}$, $\gamma = 103.379(4)^{\circ}$, V = 3177.3(4) Å³; Z = 2; $\mu = 1.968$ mm⁻¹; $\rho_{\text{ber.}} = 1.214$ g cm⁻³; 65125 reflections ($2\theta_{\text{max}} \text{ v} = 56.6^{\circ}$), 15491 unique ($R_{\text{int}} = 0.0484$); 577 parameters; largest max./min. in the final difference Fourier synthesis 0.859 e Å⁻³/-0.547 e Å⁻³; max./min. transmission 0.79/0.65; $R_1 = 0.0408$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1204. The elemental cell also contains three n-pentane molecules (carbon atoms C(71) to C(95)), which are disordered over two sites with SOF 0.5 together with the riding hydrogen atom.

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Supporting Information Available: Tables, text, thermal ellipsoid plots, and a CIF file giving X-ray crystallographic data of 1, 3, and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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