Insertion Reactions of Heterocumulenes into Zn-C Bonds: Synthesis and Structural Characterization of Multinuclear Zinc Amidate Complexes

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Summary: Reactions of ZnMe_2 with isocyanates RNCO proceeded with insertion of the isocyanate into the Zn-Me bond, yielding the corresponding heteroleptic amidate complexes $[\text{MeZnOC}(\text{Me})\text{NR}]_x$ ($\text{R} = i\text{-Pr}$ **1**, $t\text{-Bu}$ **2**) and $[\{\text{MeZn}\}_4\text{Zn}\{\text{OC}(\text{Me})\text{NC}_6\text{F}_5\}_6]$ **3** in high yields. In contrast, ZnCp^*_2 reacts with isocyanates and isothiocyanates with formation of the homoleptic complexes of the type $[\text{Zn}\{\text{OC}(\text{Cp}^*)\text{NR}\}_2]_2$ ($\text{R} = \text{Et}$ **4**, $i\text{-Pr}$ **5**) and $[\text{Zn}\{\text{SC}(\text{Cp}^*)\text{Ni-Pr}\}_2]_2$ **6**. **1 - 6** were characterized by elemental analyses, multinuclear NMR (^1H , ^{13}C , ^{19}F) and IR spectroscopy and by single-crystal X-ray diffraction (**1**, **2**, **5**).

Introduction. Metal alkyl complexes of the type L_nMR typically react with carbodiimides $C(NR)_2$ with insertion of the carbodiimide into the metal-carbon bond and subsequent formation of metal amidinate complexes of the general type $RC(NR')_2ML_n$.¹ Numerous complexes including main group metals, transition metals and lanthanide metals have been prepared and their potential capability to serve as precursors in catalysis² and material sciences³ was demonstrated. We started only recently to investigate reactions of zinc dialkyls with carbodiimides, which surprisingly had not been investigated before, in more detail. In remarkable contrast to the reaction of $ZnEt_2$ with $C(Ni-Pr)_2$, which occurred with insertion of the carbodiimide into the $Zn-Et$ bond and subsequent formation of the expected amidinate complex $[\{EtC(Ni-Pr)_2\} ZnEt]_2$,⁴ we found that $ZnMe_2$ reacts with carbodiimides such as $C(Ni-Pr)_2$ and $C(NCy)_2$ with C-H activation of the initially-formed C-Me group and formation of multinuclear amidinate complexes (Scheme 1).⁵ In contrast, no reaction occurred with carbodiimides containing sterically more demanding substituents such as 2,6-*i*-Pr₂-C₆H₃, *t*-Bu and SiMe₃, respectively.^{5b} In order to investigate if the unexpected CH-activation reaction is restricted to reactions of carbodiimides with $ZnMe_2$, we reinvestigated reactions of $C(Ni-Pr)_2$ with different main group metal alkyls such as AlMe₃, GaMe₃, MgMe₂ and MeLi at temperatures up to 120 °C and reaction times up to 10 days, but no indication for a C-H activation reaction was found.⁶

((Scheme 1 here))

We therefore became interested in reactions of ZnMe_2 with isoelectronic heterocumulenes of the type $\text{Y}=\text{C}=\text{X}$ in order to clarify, if the C-H activation reaction also occurs with these organic substrates. Insertion reactions of isocyanates $\text{RN}=\text{C}=\text{O}$ into metal-carbon as well as metal-hydrogen, metal-nitrogen and metal-oxygen bonds of main group metals,⁷ transition metals⁸ and lanthanides⁹ have been intensely studied in the past and a large number of complexes have been structurally characterized.¹⁰ In contrast, insertion reactions of isocyanates into zinc-carbon bonds have been investigated to a far lesser extent,¹¹ whereas those into zinc-hydrogen, zinc-amide and zinc-alkoxide complexes are more common.¹² To date, only a very few zinc amidate complexes, which were typically prepared by an alternate alkane elimination reaction of ZnR_2 with carboxylic amides,¹³ have been structurally characterized. These complexes, which are typically tetrameric in the solid state as was already suggested by Coates and Ridley,¹¹ typically show the amidate moieties in a N,O-bridging coordination mode with the O atoms coordinating to adjacent Zn atoms.

Herein we report on reactions of ZnMe_2 and ZnCp^*_2 with several isocyanates RNCO ($\text{R} = \text{Et}$, *i*-Pr, *t*-Bu, C_6F_5) and isothiocyanates RNCS containing organic substituents of different steric bulk and electronic properties. The resulting complexes **1** – **6** were characterized by multinuclear NMR and IR spectroscopy, elemental analyses and single crystal X-ray diffraction (**1**, **2**, **5**).

Results and Discussion. Equimolar amounts of ZnMe_2 and RNCO react at 80 °C with insertion of the isocyanate into one Zn-Me bond and subsequent formation of the corresponding heteroleptic amidate complexes $[\text{MeZnOC}(\text{Me})\text{NR}]_x$ ($\text{R} = i\text{-Pr}$ **1**, *t*-Bu **2**) in almost quantitative yields. Comparable insertion products were obtained from reactions of a β -diketiminato zinc hydride complex with carbodiimides and isocyanates, respectively.¹⁴ Homoleptic complexes $[\text{Zn}\{\text{OC}(\text{Me})\text{NR}\}_2]$ were not formed, even in the presence of a threefold excess of the isocyanate and at higher reaction temperatures (120 °C). Moreover, no indication for a C-H activation reaction of the methyl group bound to the isocyanate-carbon

atom, as was previously observed in reactions of ZnMe_2 with carbodiimides, was found, even after prolonged reaction times (10 d) and high reaction temperatures (up to 130 °C).¹⁵ In contrast, the reaction with $\text{C}_6\text{F}_5\text{NCO}$ yielded the unexpected complex $[\{\text{MeZn}\}_4\text{Zn}\{\text{OC}(\text{Me})\text{N}(\text{C}_6\text{F}_5)\}_6] \mathbf{3}$.

((Scheme 2 here))

^1H and ^{13}C NMR spectra of **1** and **2** showed the expected resonances of the heteroleptic complexes due to the amidate ligand and the Zn-Me group in the expected 1:1 molar ratio. The characteristic NCO absorption bands as observed for the isocyanates at 2245 cm^{-1} (*t*-BuNCO), 2251 cm^{-1} (*i*-PrNCO) and 2255 cm^{-1} ($\text{C}_6\text{F}_5\text{NCO}$) are shifted to 1572 cm^{-1} (**1**), 1577 cm^{-1} (**2**), and 1504 cm^{-1} (**3**), respectively.

Single-crystals of **1** and **2** were obtained from solutions in toluene upon storage at -30 °C.

((Figures 1 and 2 here))

1 and **2** crystallize in the triclinic space group *P*-1. The degree of oligomerization and the specific coordination mode of the amidate ligand within the resulting complexes is largely influenced by the steric demand of the isocyanate substituent. The larger *t*-Bu group favors the formation of the trimeric complex **2**, whereas the sterically less demanding *i*-Pr groups lead to the formation of the tetrameric complex **1**. Moreover, the coordination mode of the amidate moieties as observed in **1** and **2** differ significantly. **1** consists of two eight-membered rings (top and bottom in Fig. 1), in which the amidate groups serve as N,O-bridging monodentated (μ - η^1 - η^1) donor ligands. The Zn-N bond lengths (mean Zn-N 2.027(3) Å) within these rings are shorter than the Zn-O bonds (mean Zn-O 2.080(7) Å) as was observed for comparable zinc amidate complexes.^{13b} These two *boat-type* eight-membered rings are fused by four additional Zn-O-bonds. The Zn-O bond lengths between the two rings (mean Zn-O 2.056(3) Å) are slightly shorter compared to the Zn-O bond lengths within the eight-membered rings as was previously reported for tetrameric complexes of the desired type.^{13b} In contrast, the coordination mode of the amidate ligands in **2** can be best described as being in between an N,O-chelating (η^2) and N,O-bridging monodentated (μ - η^1 - η^1) fashion. The Zn-N (mean Zn-N 2.031(7) Å) and Zn-O bond lengths (mean Zn-O 2.011(6) Å) within the puckered 12-membered ring are almost identical. As was observed for **1**, each O atom adopts a trigonal-planar coordination sphere due to the coordination to an adjacent Zn atom. Even though these Zn-O bond lengths (mean Zn-O 2.233(3) Å) are significantly elongated compared to those within the 12-membered ring, they clearly indicate attractive Zn-O interaction. Therefore, **2** represents the first structurally characterized zinc complex exhibiting an N,O-chelating amidate ligand. A comparable structural motif was previously observed in zinc pyridonate and 9-isobutylguanidinate complexes.¹⁶ The Zn atoms in **1** and **2** adopt tetrahedral coordination spheres and the Zn-C bond lengths as observed in **1** (mean value 1.974 Å) and **2** (mean value 1.957 Å) are comparable and in the typical range reported for Zn-Me groups. The O, C and N atoms of the amidate moieties in **1** and **2** adopt almost ideal trigonal-planar

coordination spheres and the C-O (mean values: **1** 1.302; **2** 1.310 Å) and C-N bond lengths (mean values: **1** 1.295(2); **2** 1.289(2) Å) within the amidate groups indicate an almost perfect delocalization of the π -electrons within the NCO moieties.

((Figure 3 here))

Complex **3** adopts a rather unexpected structure in the solid state. Single-crystals of **3** were obtained from solutions in dichloromethane upon storage at -30 °C. Unfortunately, crystals of **3** which were obtained from different solutions were of rather poor quality and the resulting structure-model didn't allow a detailed discussion of the structural parameters. However, the connectivity of the compound was determined without ambiguity. **3** consists of five Zn atoms

and six amidate ligands. The structure can be best described as a twelve-membered $[\text{MeZnOC}(\text{Me})\text{NC}_6\text{F}_5]_3$ ring with three N,O-chelating amidate moieties, in which the three O-atoms bind to an additional Zn atom. This central Zn atom coordinates to three additional O-atoms of a $\text{MeZn}[\text{OC}(\text{Me})\text{NC}_6\text{F}_5]_3$ moiety, hence adopting a distorted octahedral coordination sphere. Obviously, the formation of **3** occurred through single insertion reactions of four isocyanates into four ZnMe_2 molecules, whereas the fifth ZnMe_2 molecule underwent a double insertion reaction with two isocyanates.

In order to investigate the isocyanate reaction in more detail and to verify the role of the organozinc complex, we reacted isocyanates and isothiocyanates with ZnCp^*_2 in both equimolar amounts and with a twofold excess of the isocyanates. Homoleptic complexes of the general type $[\text{Zn}\{\text{OC}(\text{Cp}^*)\text{NR}\}_2]_2$ ($\text{R} = \text{Et}$ **4**, *i*-Pr **5**) and $[\text{Zn}\{\text{SC}(\text{Cp}^*)\text{Ni-Pr}\}_2]_2$ **6** were obtained in both reactions at relatively low temperature (60 °C), demonstrating the double insertion reaction of isocyanates and isothiocyanates into the Zn-Cp* group to be strongly favored.¹⁷

((Scheme 3 here))

¹H and ¹³C NMR spectra of **4** - **6** only showed a single set of resonances due to the amidate and thioamidate ligands. No indication for the presence of differently coordinated amidates (η^2 -chelating and bridging $\mu\text{-}\eta^1\text{-}\eta^1$ moieties) was found in these spectra. Low-temperature ¹H NMR spectra at -60 °C also did not give two set of resonances. IR spectra of the free ligands show strong absorption bands at 2253 (EtNCO), 2251 (*i*-PrNCO) and 2148 (*i*-PrNCS) cm^{-1} due to the antisymmetric NCO- and NCS-valence vibration. In the complexes **4**, **5** and **6** these

absorption bands are shifted to 1552 (**4**), 1542 (**5**) and 1518 (**6**) cm^{-1} , respectively, as was observed for the Zn amidate complexes **1** - **3**.

((Figure 4 here))

Single-crystals of **5** were obtained from a solution in di-*iso*-propylbenzene upon storage at 0 °C. **5** crystallizes in the triclinic space group *P*-1. Central structural motif in **5** is the eight-membered $\text{Zn}_2(\text{NCO})_2$ ring with two N,O-bridging monodentate (μ - η^1 - η^1) amidate groups. Both Zn atoms in **5** are additionally coordinated by a second amidate group, which adopts a chelating (η^2) binding mode. The eight-membered ring adopts a *boat-type* conformation due to the presence of rather weak transannular Zn-O interactions (Zn1-O1 2.665; Zn2-O2 2.677 Å) as was observed in the amidinate complex $\{[\text{EtC}(\text{Ni-Pr})_2]\text{ZnEt}\}_2$ (2.669(1), 2.653(1) Å).⁴ In contrast, the heteroleptic amidinate complexes $\{[t\text{-BuC}(\text{Ni-Pr})_2]\text{ZnX}\}_2$ (X = Me, I) showed

significantly stronger transannular Zn-N interactions (2.1952(11), 2.136(3) Å).¹⁸ The Zn-N bond lengths within the eight-membered (mean value 1.9646(20) Å) and four-membered rings (mean value 1.9848(37) Å) are comparable whereas the Zn-O bond lengths within the eight-membered ring (mean value 1.9529(19) Å) are significantly shorter than those within the four-membered rings (mean value 2.1560(61) Å). As a consequence, the π -electrons within the η^2 -chelating amidate units rings (mean values C-O 1.281(2); C-N 1.311(2) Å) are rather localized. In contrast, the π -electrons within the bridging μ - η^1 - η^1 amidate moiety (mean values C-O 1.294(2); C-N 1.296(2) Å) are fully delocalized as is indicated by the almost identical C-O and C-N bond lengths. These findings most likely can be explained by repulsive interaction between the sterically demanding organic substituents.

Even though complexes **1** – **6** represent rare examples of structurally characterized dimeric, trimeric and tetrameric zinc amidate complexes, comparable cage-type organozinc complexes have been previously synthesized with different organic ligands. Zinc alkoxides for instance are long known to adopt dimeric and tetrameric structures in the solid state,¹⁹ whereas trimeric derivatives have only very recently been reported.²⁰ The same is true for zinc carboxylates and carbamates, which have also been structurally characterized to some extent.²¹ Moreover, Mitzel, Redshaw, Lewiński and others have reported in the last decade on the synthesis of comparable zinc complexes using 1,2-double donor systems such as peroxides, hydrazides as well as hydroxylamides.²² In addition, reactions of zinc alkyls with aminoalcohols proceeded with formation of a large variety of complexes including trimeric derivatives.²³

Conclusion. ZnMe₂ reacts with isocyanates with insertion into one Zn-Me bond and subsequent formation of heteroleptic amidate zinc complexes [MeZnOC(Me)NR]_x. The degree of oligomerization strongly depends on the steric bulk of the organic ligand bound to the nitrogen atom. No indication for C-H activation reactions as was observed for reactions of ZnMe₂ with carbodiimides was found. In contrast, zirconocene Cp*₂Zr reacts with isocyanates

and isothiocyanates with subsequent formation of homoleptic complexes of the type $[\text{Zn}\{\text{XC}(\text{Cp}^*)\text{NR}\}_2]_2$ ($\text{X} = \text{O}, \text{S}$).

Experimental Details. All manipulations were performed in a Glovebox (MBraun) under an Ar atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. ZnCp^*_2 was prepared according to literature method.²⁴ A 1.2 M solution of ZnMe_2 was obtained from Acros and used as received, whereas isocyanates RNCO and $i\text{-PrNCS}$ were distilled and carefully dried over activated molecular sieves prior to use. A Bruker DMX 300 was used for NMR spectroscopy. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR spectra were referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$) and $\text{THF-}d_8$ (^1H : $\delta = 3.580, 1.730$; ^{13}C : $\delta = 25.2, 67.4$). IR spectra were recorded on a Bruker ALPHA-T FT-IR spectrometer equipped 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 Duisburg-Essen.

General experimental procedure for the synthesis of 1 - 3: ZnMe_2 (4.2 mL, 5 mmol) was added to a solution of the isocyanate (5 mmol) in 20 mL of toluene and heated at 80 °C for 3 days. The resulting solution was concentrated in vacuum and stored at -30 °C. Colorless crystals of **1 - 3** were formed within 12 h.

[MeZnOC(Me)Ni-Pr]₄ 1: Yield 3.43 g (95 %). Melting point: 184 °C. Anal. Found (calcd) for $\text{C}_{24}\text{H}_{52}\text{N}_4\text{O}_4\text{Zn}_4$ (722.18 g/mol): H, 7.3 (7.3); C, 39.9 (39.9); N, 7.8 (7.8). ^1H NMR (300 MHz, C_6D_6 , 25 °C): $\delta = -0.36$ (s, 3H, ZnCH_3), 1.51 (d, 6H, $\text{CH}(\text{CH}_3)_2$), 1.71 (s, 3H, CH_3), 3.18 (sept, $^3J_{\text{HH}} = 6.4$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C): $\delta = -12.3$ (ZnCH_3), 20.0 ($\text{CH}(\text{CH}_3)_2$), 24.0 (CH_3), 50.0 ($\text{CH}(\text{CH}_3)_2$), 175.2 (NCO). IR: $\nu = 2968, 2929, 2894, 2871, 2825, 1577, 1452, 1423, 1381, 1365, 1334, 1172, 1126, 1034, 999, 829, 645, 616, 575, 556, 515\text{ cm}^{-1}$.

[MeZnOC(Me)Nt-Bu]₃ 2: Yield 2.66 g (91 %). Melting point: 188 °C. Anal. Found (calcd) for C₂₁H₄₅N₃O₃Zn₃ (583.71 g/mol): H, 7.8 (7.8); C, 43.1 (43.2); N, 7.1 (7.2). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = -0.26 (s, 3H, ZnCH₃), 1.08 (s, 9H, C(CH₃)₃), 1.89 (s, 3H, CH₃). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ = -14.3 (ZnCH₃), 20.5 (CH₃), 30.9 (C(CH₃)₃), 50.6 (C(CH₃)₃), 173.6 (NCO). IR: ν = 2974, 2901, 2832, 1572, 1466, 1381, 1363, 1339, 1214, 1162, 1154, 1064, 1033, 999, 846, 788, 667, 615, 594, 573, 530, 489, 407 cm⁻¹.

[{MeZn}₄Zn{OC(Me)NC₆F₅}₆] 3: ZnMe₂ (4.2 mL, 5 mmol) was added to a solution of the isocyanate (5 mmol) in 20 mL of toluene and heated at 80 °C for 3 days. The suspension was filtered and the resulting solid was recrystallized from a solution in CH₂Cl₂ at -30 °C. Colorless crystals of **3** were formed within 24 h.

Yield 4.9 g (70 %). Melting point: > 220 °C. Anal. Found (calcd) for C₅₃H₃₃N₆F₃₀O₆Zn₅ (1746.69 g/mol): H, 2.0 (1.9); C, 36.4 (36.4); N, 4.9 (4.8). ¹H NMR (300 MHz, THF-d₈, 25 °C): δ = -0.94 (s, 12H, ZnCH₃), 1.81 (s, 6H, CH₃), 2.11 (s, 12H, CH₃). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ = 1.4 (ZnCH₃), 21.0 (CH₃), 137.1 (Ar-C), 140.5 (Ar-C), 141.9 (Ar-C), 145.2 (Ar-C), 182.3 (NCO). ¹⁹F NMR (300 MHz, C₆D₆, 25 °C): -147.1, -149.0, -162.8, -164.3, -165.6. IR: ν = 2963, 1573, 1504, 1410, 1259, 1085, 1020, 989, 88, 792, 712, 656, 539, 505, 399 cm⁻¹.

General experimental procedure for the synthesis of 4 - 6: A solution of the isocyanate RNCO (2 mmol) or the isothiocyanate *i*-PrNCS (2 mmol) in 5 mL of toluene was added to a solution of ZnCp*₂ (0.34 g, 1 mmol) in 20 mL of toluene and heated at 60 °C for 3 h. The resulting solution was concentrated in vacuum and stored at 0 °C. Colorless crystalline solids of **4 - 6** were formed within 12 h.

[Zn{OC(Cp*)NEt}₂]₂ 4: Yield 0.43 g (89 %). Melting point: 257 °C. Anal. Found (calcd) for C₅₂H₈₀N₄O₄Zn₂ (955.98 g/mol): H, 8.4 (8.4); C, 64.4 (65.3); N, 5.4 (5.9). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.15 (t, ³J_{HH} = 7.2 Hz, 3H, CH₂CH₃), 1.58 (s, 3H, C₅Me₅), 1.68 (s,

6H, C_5Me_5), 1.96 (s, 6H, C_5Me_5), 2.95 (q, $^3J_{HH} = 7.2$ Hz, 2H, CH_2CH_3). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C): $\delta = 10.3$ (C_5Me_5), 11.2 (C_5Me_5), 18.2 (C_5Me_5), 23.2 (CH_3), 34.2 (CH_2), 65.6 (C_5Me_5), 136.3 (C_5Me_5), 140.1 (C_5Me_5), 171.0 (NCO). IR: $\nu = 2966, 2913, 2853, 1552, 1520, 1442, 1395, 1333, 1281, 1261, 1174, 1086, 1064, 952, 894, 806, 723, 668, 639, 577, 511, 446$ cm^{-1} .

[Zn{OC(Cp*)Ni-Pr}₂]₂ 5: Yield 0.48 g (94 %). Melting point: >300 °C. Anal. Found (calcd) for $C_{56}H_{88}N_4O_4Zn_2$ (1012.08 g/mol): H, 8.7 (8.8); C, 64.7 (66.5); N, 4.4 (5.5). 1H NMR (300 MHz, C_6D_6 , 25 °C): $\delta = 1.18$ (d, $^3J_{HH} = 6.2$ Hz, 6H, $CH(CH_3)_2$), 1.60 (s, 3H, C_5Me_5), 1.69 (s, 6H, C_5Me_5), 1.99 (s, 6H, C_5Me_5), 3.41 (sept, $^3J_{HH} = 6.0$ Hz, 1H, $CH(CH_3)_2$). ^{13}C NMR (125 MHz, C_6D_6 , 25 °C): $\delta = 10.2$ (C_5Me_5), 11.0 (C_5Me_5), 23.8 (C_5Me_5), 26.4 (CH_3), 49.9 (CH), 66.1 (C_5Me_5), 135.3 (C_5Me_5), 140.1 (C_5Me_5), 175.4 (NCO). IR: $\nu = 2962, 2914, 2856, 1542, 1516, 1462, 1441, 1408, 1395, 1377, 1360, 1325, 1260, 1172, 1089, 1056, 1012, 872, 799, 730, 695, 682, 634, 575, 512, 463, 428$ cm^{-1} .

[Zn{SC(Cp*)Ni-Pr}₂]₂ 6: Yield 0.34 g (63 %). Melting point: 189 °C. Anal. Found (calcd) for $C_{56}H_{88}N_4S_4Zn_2$ (1076.33 g/mol): H, 8.1 (8.2); C, 60.2 (62.5); N, 4.8 (5.2); S 10.4 (11.9). 1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.85$ (d, $^3J_{HH} = 6.1$ Hz, 6H, $CH(CH_3)_2$), 1.36 (s, 3H, C_5Me_5), 1.74 (s, 6H, C_5Me_5), 1.82 (s, 6H, C_5Me_5), 3.21 (sept, $^3J_{HH} = 6.1$ Hz, 1H, $CH(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): $\delta = 10.6$ (C_5Me_5), 11.1 (C_5Me_5), 24.1 (C_5Me_5), 26.9 (CH_3), 50.1 (CH), 66.2 (C_5Me_5), 135.6 (C_5Me_5), 140.8 (C_5Me_5), 197.5 (NCO). IR: $\nu = 2969, 2904, 2851, 1658, 1518, 1438, 1381, 1360, 1260, 1242, 1174, 1161, 1095, 1013, 996, 934, 873, 798, 749, 630, 596, 497, 456, 442$ cm^{-1} .

Single-crystal X-ray analyses. Crystallographic data for **1**, **2** and **5**, which were collected on a Bruker AXS D8 Kappa diffractometer ($MoK\alpha$ radiation, $\lambda = 0.71073$ Å), are summarized in Table 1 and selected bond lengths and angles in Tables 2 (**1**, **2**) and 3 (**5**), respectively. **1** was measured at 100(1) K, **2** at 203(1) K and **5** at 193(1) K. The structures were solved by Direct

Methods (SHELXS-97)²⁵ and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97).²⁶ Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Baker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The poor quality of the crystal of **3** ($\theta_{\text{max}} = 23^\circ$) prevented a proper refinement of the structure model (R_1 above 0.15, no anisotropic refinement possible). However, connectivity and atom-types were determined without doubt. **5** crystallizes with one molecule di-isopropylbenzene disorderd over a centre of inversion. The corresponding carbon atoms were refined isotropically and the phenyl ring was constraint to be a regular hexagon (AFIX 66).

The crystallographic data of the structures (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-794411 (**1**), CCDC-794410 (**2**) and CCDC-802042 (**5**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code_(1223)336-033; Email for inquiry: fileserv@ccdc.cam.ac.uk; E-Mail for deposition: deposit@ccdc.cam.ac.uk).

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Figure / Scheme Captions

Figure 1. Solid-state structure of **1** (thermal ellipsoids are shown at 50 % probability levels; H atoms are omitted for clarity).

Figure 2. Solid-state structure of **2** (thermal ellipsoids are shown at 50 % probability levels; H atoms are omitted for clarity).

Figure 3. Solid-state structure of **3** (thermal ellipsoids are shown at 50 % probability levels; H atoms are omitted and C₆F₅ groups and Me amidate groups are presented in a diminished fashion for clarity).

Figure 4. Solid-state structure of **5** (thermal ellipsoids are shown at 50 % probability levels; H atoms are omitted for clarity).

Scheme 1. Different reaction pathways as observed for the reactions of ZnR₂ with *iso*-propylcarbodiimide.

Scheme 2. Synthesis of **1** - **3**.

Scheme 3. Synthesis of **4** - **6**.

TABLES.

Table 1. Crystallographic details for complexes **1**, **2**, and **5**.

	1	2	5
Empirical formula	C ₂₄ H ₅₂ N ₄ O ₄ Zn ₄	C ₂₁ H ₄₅ N ₃ O ₃ Zn ₃	C ₅₆ H ₈₈ N ₄ O ₄ Zn ₂ x 0.5 C ₁₂ H ₁₈
Molecular mass	722.18	583.71	1093.18
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
T [K]	100(1)	203(1)	193(1)
a [Å]	11.3409(5)	9.0753(4)	13.2153(7)
b [Å]	11.8633(5)	12.3820(5)	13.5886(8)
c [Å]	13.2487(5)	14.3193(6)	18.7837(11)
α [°]	74.605(2)	75.062(2)	79.754(3)
β [°]	82.448(2)	76.264(2)	86.258(3)
γ [°]	76.447(2)	71.623(2)	72.867(3)
V [Å ³]	1666.11(12)	1453.84(11)	3171.7(3)
Z	2	2	2
μ [mm ⁻¹]	2.876	2.477	0.801
D _{calcd.} [g cm ⁻³]	1.440	1.333	1.145
Crystal dim. [mm]	0.36 x 0.32 x 0.25	0.36 x 0.32 x 0.26	0.28 x 0.24 x 0.17
No. of reflections	22481	17582	29180
No. of unique reflections	8223	5350	14253
R _{merg}	0.0225	0.0190	0.0175
No. param. refined / restraints	325 / 0	271 / 0	631 / 0
R ₁	0.0197	0.0283	0.0375
wR ₂	0.0515	0.0767	0.1068
Goodness of fit ^[c]	1.085	1.059	1.016
Final max/min. Δρ, e Å ⁻³	0.484 / -0.454	0.510 / -0.258	0.632 / -0.498

^[a] $RI = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). - ^[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for all data). Goodness of fit = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [deg] of **1** and **2**.

1							
Zn(1)-N(31)	2.0198(12)	Zn(1)-C(6)	1.9778(15)	Zn(3)-O(11)	2.0541(9)	O(21)-C(21)	1.3011(16)
Zn(2)-N(11)	2.0224(12)	Zn(2)-C(16)	1.9709(16)	Zn(4)-O(21)	2.0658(10)	O(31)-C(31)	1.3044(17)
Zn(3)-N(21)	2.0308(11)	Zn(3)-C(26)	1.9687(14)	N(31)-Zn(1)-O(21)	100.35(4)	C(11)-O(11)-Zn(4)	125.42(8)
Zn(4)-N(1)	2.0357(12)	Zn(4)-C(36)	1.9775(14)	N(11)-Zn(2)-O(1)	98.17(4)	N(11)-C(11)-O(11)	119.64(12)
Zn(1)-O(21)	2.0815(9)	N(1)-C(1)	1.2958(18)	N(21)-Zn(3)-O(31)	97.90(4)	C(21)-N(21)-Zn(3)	119.79(9)
Zn(2)-O(1)	2.1007(10)	N(11)-C(11)	1.2956(18)	N(1)-Zn(4)-O(11)	98.44(4)	C(21)-O(21)-Zn(1)	124.25(8)
Zn(3)-O(31)	2.0720(10)	N(21)-C(21)	1.2950(17)	C(1)-N(1)-Zn(4)	119.08(10)	N(21)-C(21)-O(21)	120.38(12)
Zn(4)-O(11)	2.0652(9)	N(31)-C(31)	1.2940(18)	C(1)-O(1)-Zn(2)	127.08(9)	C(31)-N(31)-Zn(1)	119.84(10)
Zn(1)-O(1)	2.0551(10)	O(1)-C(1)	1.2989(17)	N(1)-C(1)-O(1)	120.35(12)	C(31)-O(31)-Zn(3)	131.14(8)
Zn(2)-O(31)	2.0485(10)	O(11)-C(11)	1.3046(16)	C(11)-N(11)-Zn(2)	119.60(9)	N(31)-C(31)-O(31)	119.48(12)
2							
Zn(1)-N(1)	2.031(2)	Zn(1)-C(7)	1.958(3)	Zn(3)-O(3)	2.0008(18)	N(3)-C(21)	1.292(3)
Zn(2)-N(2)	2.048(2)	Zn(2)-C(17)	1.954(3)	N(1)-Zn(1)-O(1)	61.94(8)	Zn(3)-O(1)-Zn(1)	133.87(9)
Zn(3)-N(3)	2.015(2)	Zn(3)-C(27)	1.959(3)	N(2)-Zn(2)-O(2)	61.63(8)	Zn(1)-O(2)-Zn(2)	134.58(9)
Zn(1)-O(1)	2.1953(18)	O(1)-C(1)	1.315(3)	N(3)-Zn(3)-O(3)	60.70(7)	Zn(2)-O(3)-Zn(3)	119.37(8)
Zn(2)-O(2)	2.2017(18)	O(2)-C(11)	1.309(3)	O(2)-Zn(1)-O(1)	89.13(7)	N(1)-C(1)-O(1)	113.9(2)
Zn(3)-O(3)	2.3032(18)	O(3)-C(21)	1.307(3)	O(3)-Zn(2)-O(2)	92.75(7)	N(2)-C(11)-O(2)	114.1(2)
Zn(1)-O(2)	2.0078(18)	N(1)-C(1)	1.285(3)	O(1)-Zn(3)-O(3)	95.46(7)	N(3)-C(21)-O(3)	115.3(2)
Zn(2)-O(3)	2.0237(18)	N(2)-C(11)	1.290(4)				

Table 3. Selected bond lengths [Å] and angles [deg] of **5**.

5			
Zn(1)-N(1)	1.9622(16)	Zn(2)-C(4)	2.4436(19)
Zn(1)-N(3)	1.9798(16)	N(1)-C(1)	1.293(2)
Zn(2)-N(2)	1.9670(15)	O(1)-C(1)	1.292(2)
Zn(2)-N(4)	1.9898(16)	N(2)-C(2)	1.298(2)
Zn(1)-O(2)	1.9552(11)	O(2)-C(2)	1.296(2)
Zn(1)-O(3)	2.1685(14)	N(3)-C(3)	1.312(3)
Zn(2)-O(1)	1.9506(13)	O(3)-C(3)	1.282(2)
Zn(2)-O(4)	2.1514(14)	N(4)-C(4)	1.309(3)
Zn(1)-C(3)	2.4515(19)	O(4)-C(4)	1.280(2)
N(1)-Zn(1)-O(2)	118.84(6)	N(4)-Zn(2)-O(1)	117.49(6)
N(1)-Zn(1)-N(3)	124.84(7)	O(1)-Zn(2)-O(4)	104.18(5)
N(3)-Zn(1)-O(2)	112.86(6)	N(2)-Zn(2)-O(4)	119.92(6)
O(2)-Zn(1)-O(3)	103.93(6)	N(4)-Zn(2)-O(4)	63.83(6)
N(1)-Zn(1)-O(3)	117.64(6)	N(1)-C(1)-O(1)	117.61(16)
N(3)-Zn(1)-O(3)	63.64(6)	N(2)-C(2)-O(2)	117.80(17)
N(2)-Zn(2)-O(1)	116.16(6)	N(3)-C(3)-O(3)	115.40(17)
N(2)-Zn(2)-N(4)	122.40(7)	N(4)-C(4)-O(4)	115.85(17)

References

- [1] See the following and references cited therein: (a) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219. (b) Edelmann, F. T.; Coles, M. P. *J. Chem. Soc. Dalton Trans.* **2006**, 985. (c) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 133-352. (d) Edelmann, F. T. *Chem. Soc. Rev.* **2009**, *38*, 2253.
- [2] (a) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; *Organometallics* **1997**, *16*, 5183. (b) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (c) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (d) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2000**, *39*, 924.
- [3] (a) Barker, J.; Blacker, N. C.; Phillips, N. C.; Alcock, N. W.; Errington, W.; Wallbridge, M. G. H. *J. Chem. Soc. Dalton Trans.*, **1996**, 431. (b) Baunemann, A.; Bekermann, D.; Thiede, T. B.; Parala, H.; Winter, M.; Gemel, C.; Fischer, R. A. *J. Chem. Soc. Dalton Trans.* **2008**, 3715.
- [4] Schulz, S.; Münch, M.; Flörke, U. *Z. Anorg. Allg. Chem.* **2008**, *634*, 2221.
- [5] (a) Münch, M.; Flörke, U.; Bolte, M.; Schulz, S.; Gudat, D. *Angew. Chem.* **2008**, *120*, 1535; *Angew. Chem., Int. Ed.* **2008**, *47*, 1512. (b) Schmidt, S.; Gondzik, S.; Schulz, S.; Bläser, D.; Boese, R. *Organometallics* **2009**, *28*, 4371.
- [6] Gutschank, B.; Schmidt, S.; Schulz S. unpublished results.
- [7] (a) Chang, C.-C.; Chen, J.-H.; Srinivas, B.; Chiang, M. Y.; Lee, G.-H.; Peng, S.-M. *Organometallics* **1997**, *16*, 4980. (b) Tsai, C.-F.; Chen, H.-J.; Chang, J.-C.; Hung, C.-H.; Lai, C.-C.; Hu, C.-H.; Huang, J.-H. *Inorg. Chem.* **2004**, *4*, 2183. (c) Peng, Y.; Bai, G.; Fan, H.; Vidovic, D.; Roesky, H. W.; Magull, J. *Inorg. Chem.*, **2004**, *43*, 1217. (d)

- Chen, I.-C.; Ho, S.-M.; Chen, Y.-C.; Lin, C.-Y.; Hu, C.-H.; Tu, C.-Y.; Datta, A.; Huang, J.-H.; Lin, C.-H. *J. Chem. Soc. Dalton Trans.* **2009**, 8631.
- [8] (a) Weiss, K.; Schubert, U.; Schrock, R. R. *Organometallics* **1986**, *5*, 397. (b) Cowan, R. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4750. (c) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1994**, *13*, 569. (d) Gately, D. A.; Norton, J. R.; Goodson, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 986. (e) Srinivas, B.; Chang, C. C.; Chen, C. H.; Chiang, M. Y.; Chen, I. T.; Wang, Y.; Lee, G. H. *J. Chem. Soc. Dalton Trans.* **1997**, 957. (f) Hsieh, K.-C.; Lee, W.-Y.; Lai, C.-L.; Hu, C.-H.; Lee, H. M.; Huang, J.-H.; Peng, S.-M.; Lee G.-H. *J. Organomet. Chem.* **2004**, *689*, 3362. (g) Ghoshm, R.; Nethaji, M.; Samuelson, A. G. *J. Organomet. Chem.* **2005**, *690*, 1282. (h) Kumar, A.; De, S.; Samuelson, A. G.; Jemmis, E. D. *Organometallics* **2008**, *27*, 955.
- [9] (a) Zhou, X.; Zhang, L.; Zhu, M.; Cai, R.; Weng, L. *Organometallics* **2001**, *20*, 5700. (b) Zhang, J.; Cai, R.; Weng, L.; Zhou, X. *Organometallics*, **2003**, *22*, 5385. (c) Tardif, O.; Hashizume, D.; Hou, Z. *J. Am. Chem. Soc.* **2004**, *12*, 8080. (d) Sun, Y.; Zhang, Z.; Wang, X.; Li, X.; Weng, L.; Zhou X. *Organometallics* **2009**, *28*, 6320.
- [10] Reviews: (a) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927. (b) Evans, W. J.; Davis, B. L. *Chem. Rev.* **2002**, *102*, 2119. (c) Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787.
- [11] Coates, G. E.; Ridley, D. *J. Chem. Soc. A* **1966**, 1064.
- [12] See the following and references cited therein: (a) Han, R.; Gorrell, I. B.; Looney A. G.; Parkin, G. *J. Chem. Soc. Chem. Commun.* **1991**, 717. (b) Rombach, M.; Brombacher H.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2002**, 153. (c) Schenk, S.; Notni, J.; Köhn, U.; Wermann, K.; Anders, E. *J. Chem. Soc. Dalton Trans.* **2006**, 4191.

- [13] (a) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1969**, *16*, 345. (b) Boss, S. R.; Haigh, R.; Linton, D. J.; Schooler, P.; Shields, G. P.; Wheatley, A. E. H. *J. Chem. Soc. Dalton Trans.* **2003**, 1001.
- [14] Schulz, S.; Eisenmann, T.; Schmidt, S.; Bläser, D.; Westphal, U.; Boese, R. *J. Chem. Soc. Chem. Commun.* **2010**, *46*, 7226.
- [15] Higher reaction temperatures resulted in the complete decomposition of ZnMe₂ and formation of elemental zinc.
- [16] (a) Mowat, C. G.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Acta Cryst.* **1997**, *C53*, 282. (b) Badura, D.; Vahrenkamp, H. *Eur. J. Inorg. Chem.* **2003**, 3723.
- [17] In the equimolar reaction unreacted ZnCp*₂ was also detected by ¹H NMR.
- [18] Schmidt, S.; Schulz, S.; Bolte, M. *Z. Anorg. Allg. Chem.* **2009**, *635*, 2210.
- [19] See the following and references cited therein: (a) Enthaler, S.; Eckhardt, B.; Inoue, S.; Irran, E.; Driess, M. *Chem. Asian J.* **2010**, *5*, 2017. (b) Jana, S.; Berger, R. J. F.; Fröhlich, R.; Pape, T.; Mitzel, N. W. *Inorg. Chem.* **2007**, *46*, 4293. (c) Polarz, S.; Strunk, J.; Ischenko, V.; van den Berg, M. W. E.; Hinrichsen, O.; Muhler, M.; Driess, M. *Angew. Chem.* **2006**, *118*, 3031; *Angew. Chem., Int. Ed.* **2006**, *45*, 2965. (d) Lewiński, J.; Śliwinski, W.; Dranka, M.; Justyniak, I.; Lipkowski, J. *Angew. Chem.* **2006**, *118*, 4944; *Angew. Chem., Int. Ed.* **2006**, *45*, 4826. (e) Kim, C. G.; Sung, K.; Chung, T. M.; Jung, D. Y.; Kim, Y. *J. Chem. Soc. Chem. Commun.* **2003**, 2068.
- [20] Lewiński, J.; Dutkiewicz, M.; Lesiuk, M.; Śliwinski, W.; Zelga, K.; Justyniak, I.; Lipkowski, J. *Angew. Chem.* **2010**, *122*, 8442; *Angew. Chem., Int. Ed.* **2010**, *49*, 8266.
- [21] (a) Redshaw, C.; Jana, S.; Shang, C.; Elsegood, M. R. J.; Lu, X.; Guo, Z. X. *Organometallics* **2010**, *29*, 6129. (b) Boyle, T. J.; Pratt, H. D. I.; Alam, T. M.;

- Headley, T.; Rodriguez, M. A. *Eur. J. Inorg. Chem.* **2009**, 855. (c) Orchard, K. L.; White, A. J. P.; Shaffer, M. S. P.; Williams, C. K. *Organometallics* **2009**, 28, 5828. (d) Redshaw, C.; Elsegood, M. R. J. *Angew. Chem.* **2007**, 119, 7597; *Angew. Chem. Int. Ed.* **2007**, 46, 7453.
- [22] (a) Lewiński, J.; Suwala, K.; Kubisiak, M.; Ochal, Z.; Justyniak, I.; Lipkowski, J. *Angew. Chem.* **2008**, 120, 8006; *Angew. Chem., Int. Ed.* **2008**, 47, 7888. (b) Lewiński, J.; Suwala, K.; Kaczorowski, T.; Galezowski, M.; Gryko, D. T.; Justyniak, I.; Lipkowski, J. *J. Chem. Soc. Chem. Commun.* **2009**, 215. (c) Jana, S.; Fröhlich, R.; Mitzel, N. W. *Z. Anorg. Allg. Chem.* **2008**, 634, 1477. (d) Elsegood, M. R. J.; Redshaw, C. *Chem. Eur. J.* **2008**, 14, 3530. (e) Redshaw, C.; Elsegood, M. R. J. *J. Chem. Soc. Chem. Commun.* **2006**, 523. (f) Jana, S.; Fröhlich, R.; Berger, R. J. F.; Mitzel, N. W. *J. Chem. Soc. Chem. Commun.* **2006**, 3993. (g) Jana, S.; Fröhlich, R.; Mitzel, N. W. *Z. Naturforsch.* **2006**, 61b, 838. (h) Jana, S.; Fröhlich, R.; Mitzel, N. W. *Eur. J. Inorg. Chem.* **2006**, 3936. (i) Jana, S.; Fröhlich, R.; Mitzel, N. W. *Chem. Eur. J.* **2006**, 12, 592. (j) Ullrich, M.; Lustig, C.; Berger, R. J. F.; Fröhlich, R.; Mitzel, N. W. *Eur. J. Inorg. Chem.* **2006**, 4219. (k) Lewiński, J.; Ochal, Z.; Bojarski, E.; Tratkiewicz, E.; Justyniak, I.; Lipkowski, J. *Angew. Chem.* **2003**, 115, 4791; *Angew. Chem. Int. Ed.* **2003**, 42, 4643.
- [23] (a) Hollingsworth, N.; Johnson, A. L.; Kingsley, A.; Kociok-Köhn, G.; Molloy, K. C. *Organometallics* **2010**, 29, 3318. (b) Hunger, J.; Blaurock, S.; Sieler, J. *Z. Anorg. Allg. Chem.* **2005**, 631, 472.
- [24] Blom, R.; Boersma, J.; Budzelaar, P. H. M.; Fischer, B.; Haaland, A.; Volden, H. V.; Weidlein, J. *Acta Chem. Scand.* **1986**, A 40, 113.
- [25] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, 46, 467.

- [26] Sheldrick, G. M. *SHELXL-97, Program for Crystal structure Refinement*; Universität Göttingen, 1997.

Graphic for Table of Content.

ZnMe_2 and ZnCp^*_2 react with isocyanates with insertion into the Zn-C bond and subsequent formation of either heteroleptic $[\text{MeZnOC}(\text{Me})\text{NR}]_x$ or homoleptic $\text{Zn}[\text{OC}(\text{Cp}^*)\text{NR}]_2$ amidate zinc complexes. The degree of oligomerization of these complexes strongly depends on the steric bulk of the organic ligand bound to the nitrogen center.

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