

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

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Reactions of ZnMe<sub>2</sub> with isocyanates RNCO proceeded with insertion of the isocyanate into the Zn–Me bond, giving the corresponding heteroleptic amidate complexes  $[MeZnOC(Me)NR]_x$  (R = *i*-Pr (1), *t*-Bu (2)) and  $[\{MeZn\}_4Zn\{OC(Me)NC_6F_5\}_6]$  (3) in high yields. In contrast,  $ZnCp^*_2$  reacts with isocyanates and isothiocyanates with formation of homoleptic complexes of the type  $[Zn\{OC(Cp^*)NR\}_2]_2$  (R = Et (4), *i*-Pr (5)) and  $[Zn\{SC(Cp^*)N-i-Pr\}_2]_2$  (6). 1–6 were characterized by elemental analyses, multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F) and IR spectroscopy, and 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')<sub>2</sub>ML<sub>n</sub>.<sup>1</sup> Numerous complexes, including main-group metals, transition metals, and lanthanide metals, have been prepared and their potential capability to serve as precursors in catalysis<sup>2</sup> 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<sub>2</sub> with C(N*i*-Pr)<sub>2</sub>, which occurred with insertion of the carbodiimide into the Zn-Et bond and subsequent formation of the expected amidinate complex [{EtC(N-i-Pr)<sub>2</sub>}ZnEt]<sub>2</sub>,<sup>4</sup> we found that ZnMe<sub>2</sub> reacts with carbodiimides such as C(N-i-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).<sup>5</sup> In contrast, no reaction occurred with carbodiimides containing sterically more demanding substituents such as 2,6-i-Pr2 $C_6H_3$ , *t*-Bu, and SiMe<sub>3</sub>, respectively.<sup>5b</sup> In order to investigate if the unexpected C–H activation reaction is restricted to reactions of carbodiimides with ZnMe<sub>2</sub>, we reinvestigated reactions of C(N-*i*-Pr)<sub>2</sub> with different main-group-metal alkyls such as AlMe<sub>3</sub>, GaMe<sub>3</sub>, MgMe<sub>2</sub>, 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.<sup>6</sup>

We therefore became interested in reactions of  $ZnMe_2$  with isoelectronic heterocumulenes of the type Y=C=X in order to clarify if the C-H activation reaction also occurs with these organic substrates. Insertion reactions of isocyanates RNCO into metal-carbon as well as metal-hydrogen, metal-nitrogen, and metal-oxygen bonds of main-group metals,<sup>7</sup> transition metals,<sup>8</sup> and lanthanides<sup>9</sup> have been intensely studied in the past, and a large number of complexes have been structurally characterized.<sup>10</sup> In contrast,

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Scheme 1. Different Reaction Pathways As Observed for the Reactions of ZnR<sub>2</sub> with Isopropylcarbodiimide



Scheme 2. Synthesis of 1-3

 $RN = C = O + ZnMe_{2} \xrightarrow{80 \ ^{\circ}C} [MeZnOC(Me)NR]_{x}$   $R = i - Pr \mathbf{1}, t - Bu \mathbf{2}$   $(C_{6}F_{5})N = C = O + ZnMe_{2} \xrightarrow{80 \ ^{\circ}C} [\{MeZn\}_{4}Zn\{OC(Me)N(C_{6}F_{5})\}_{6}] \mathbf{3}$ 

insertion reactions of isocyanates into zinc–carbon bonds have been investigated to a far lesser extent,<sup>11</sup> whereas those into zinc–hydrogen, zinc–amide, and zinc–alkoxide complexes are more common.<sup>12</sup> To date, only a very few zinc amidate complexes, which were mostly prepared by alkane elimination reactions of ZnR<sub>2</sub> with carboxylic amides,<sup>13</sup> have been structurally characterized. These complexes, which are often tetrameric in the solid state as was already suggested by Coates and Ridley,<sup>11</sup> 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 (R = Et, *i*-Pr, *t*-Bu, C<sub>6</sub>F<sub>5</sub>) 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<sub>2</sub> 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 [MeZnOC(Me)NR]<sub>x</sub> (R = *i*-Pr (1), *t*-Bu (2)) in almost quantitative yields (Scheme 2). Comparable insertion products were obtained from reactions of a  $\beta$ -diketiminato zinc hydride complex with carbodiimides and isocyanates, respectively.<sup>14</sup> Homoleptic complexes [Zn{OC(Me)NR}<sub>2</sub>] were not formed, even in the presence of a 3-fold 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<sub>2</sub> with carbodiimides, was found, even after



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

prolonged reaction times (10 days) and high reaction temperatures (up to 130 °C).<sup>15</sup> In contrast, the reaction with  $C_6F_5NCO$  yielded the unexpected complex [{MeZn}<sub>4</sub>Zn-{OC(Me)N(C\_6F\_5)}\_6] (3).

<sup>1</sup>H and <sup>13</sup>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<sup>-1</sup> (*t*-BuNCO), 2251 cm<sup>-1</sup> (*i*-PrNCO), and 2255 cm<sup>-1</sup> ((C<sub>6</sub>F<sub>5</sub>)NCO) are shifted to 1572 cm<sup>-1</sup> (1), 1577 cm<sup>-1</sup> (2), and 1504 cm<sup>-1</sup> (3), respectively.

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

1 and 2 crystallize in the triclinic space group  $P\overline{1}$ . 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 modes of the amidate moieties as observed in 1 and 2 differ significantly. 1 consists of two eight-membered rings (top and bottom in Figure 1), in which the amidate groups serve as N,O-bridging monodentate  $(\mu, \eta^1; \eta^1)$  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.<sup>13b</sup> These two boattype 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.<sup>13b</sup> In contrast, the coordination mode of the amidate ligands in 2 can be best described as being between an N,O-chelating  $(\eta^2)$  and N,O-bridging monodentate  $(\mu,\eta^1:\eta^1)$  fashion (Figure 2). The Zn-N (mean Zn-N = 2.031(7) Å) and Zn–O bond lengths (mean Zn–O = 2.011(6)A) within the puckered 12-membered ring are almost identical. As was observed for 1, each O atom adopts a trigonalplanar 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

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<sup>(15)</sup> Higher reaction temperatures resulted in the complete decomposition of  $ZnMe_2$  and formation of elemental zinc.



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



Figure 3. Solid-state structure of 3 (H atoms are omitted, and  $C_6F_5$  groups and Me amidate groups are presented in a diminished fashion for clarity).

indicate an 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.<sup>16</sup> 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 are 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 Å; **2**, 1.310 Å) and C–N bond lengths (mean values: **1**, 1.295(2) Å; **2**, 1.289(2) Å) within the amidate groups indicate an almost perfect delocalization of the  $\pi$  electrons within the NCO moieties.

Complex 3 adopts a rather unexpected structure in the solid state (Figure 3). Single crystals of 3 were obtained from solutions in dichloromethane upon storage at -30 °C. Unfortunately, crystals of 3 which were obtained from

Scheme 3. Synthesis of 4 - 6

$$RN=C=O + Cp_{2}^{*}Zn \xrightarrow{60 \ ^{\circ}C} [Zn\{OC(Cp^{*})NR\}_{2}]_{2}$$

$$R = Et 4, i \cdot Pr 5$$

$$i \cdot PrN=C=S + Cp_{2}^{*}Zn \xrightarrow{60 \ ^{\circ}C} [Zn\{SC(Cp^{*})N-i \cdot Pr\}_{2}]_{2} f$$

different solutions were of rather poor quality and the resulting structure model did not 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 12-membered [MeZnOC(Me)NC<sub>6</sub>F<sub>5</sub>]<sub>3</sub> ring with 3 N,O-chelating amidate moieties, in which the 3 O atoms bind to an additional Zn atom. This central Zn atom coordinates to three additional O atoms of a MeZn[OC-(Me)NC<sub>6</sub>F<sub>5</sub>]<sub>3</sub> moiety, hence adopting a distorted-octahedral coordination sphere. Obviously, the formation of **3** occurred through single-insertion reactions of four isocyanates into four ZnMe<sub>2</sub> molecules, whereas the fifth ZnMe<sub>2</sub> 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  $ZnCp_2^*$  both in equimolar amounts and with a 2-fold excess of the isocyanates. Homoleptic complexes of the general type  $[Zn\{OC(Cp^*)NR\}_2]_2$  (R = Et(4), i-Pr(5)) and  $[Zn\{SC(Cp^*)-N-i$ -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 (Scheme 3).<sup>17</sup>

<sup>1</sup>H and <sup>13</sup>C 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 ( $\eta^2$ -chelating and bridging  $\mu$ , $\eta^1$ : $\eta^1$  moieties) was found in these spectra. Low-temperature <sup>1</sup>H NMR spectra at -60 °C also did not give two sets of resonances. IR spectra of the free ligands show strong absorption bands at 2253 cm<sup>-1</sup> (EtNCO), 2251 cm<sup>-1</sup> (*i*-PrNCO), and 2148 cm<sup>-1</sup> (*i*-PrNCS) due to the antisymmetric NCO and NCS valence vibrations. In complexes **4**–**6** these absorption bands are shifted to 1552 cm<sup>-1</sup> (**4**), 1542 cm<sup>-1</sup> (**5**), and 1518 cm<sup>-1</sup> (**6**), respectively, as was observed for the Zn amidate complexes **1**–**3**.

Single crystals of 5 were obtained from a solution in diisopropylbenzene upon storage at 0 °C. 5 crystallizes in the triclinic space group  $P\overline{1}$  (Figure 4). The central structural motif in 5 is the eight-membered  $Zn_2(NCO)_2$  ring with two N,O-bridging monodentate  $(\mu, \eta^1; \eta^1)$  amidate groups. Both Zn atoms in 5 are additionally coordinated by a second amidate group, which adopts a chelating  $(\eta^2)$  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 A; Zn2-O2 = 2.677 A), as was observed in the amidinate complex {[EtC(N-i-Pr)<sub>2</sub>]- $ZnEt_{2}^{2}$  (2.669(1), 2.653(1) Å).<sup>4</sup> In contrast, the heteroleptic amidinate complexes { $[t-BuC(N-i-Pr)_2]ZnX$ }<sub>2</sub> (X = Me, I) showed significantly stronger transannular Zn-N interactions (2.1952(11), 2.136(3) Å).<sup>18</sup> 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 compar-

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

able, whereas the Zn–O bond lengths within the eightmembered 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  $\pi$  electrons within the  $\eta^2$ -chelating amidate units rings (mean values C–O = 1.281(2) Å and C–N = 1.311(2) Å) are rather localized. In contrast, the  $\pi$  electrons within the bridging  $\mu$ , $\eta^1$ : $\eta^1$  amidate moiety (mean values C–O = 1.294(2) Å and 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 interactions 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, have long been known to adopt dimeric and tetrameric structures in the solid state, <sup>19</sup> whereas trimeric derivatives have only very recently been reported. <sup>20</sup> The same is true for zinc carboxylates and carbamates, which have also been structurally characterized to some extent. <sup>21</sup> Moreover, Mitzel, Redshaw, Lewiński, and others have reported in the past decade on the synthesis of

comparable zinc complexes using 1,2-double-donor systems such as peroxides, and hydrazides as well as hydroxylamides.<sup>22</sup> In addition, reactions of zinc alkyls with amino alcohols proceeded with formation of a large variety of complexes, including trimeric derivatives.<sup>23</sup>

## Conclusion

ZnMe<sub>2</sub> reacts with isocyanates with insertion into one Zn–Me bond and subsequent formation of the heteroleptic amidate zinc complexes [MeZnOC(Me)NR]<sub>x</sub>. 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 were observed for reactions of ZnMe<sub>2</sub> with carbodiimides, was found. In contrast, zincocene Cp\*<sub>2</sub>Zn reacts with isocyanates and isothiocyanates with subsequent formation of homoleptic complexes of the type [Zn{XC(Cp\*)NR}<sub>2</sub>]<sub>2</sub> (X = O, 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 methods.<sup>24</sup> A 1.2 M solution of  $ZnMe_2$ was obtained from Acros and used as received, whereas isocyanates RNCO and *i*-PrNCS were distilled and carefully dried over activated molecular sieves prior to use. A Bruker DMX 300 instrument was used for NMR spectroscopy. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and  $^{19}$ F{ $^{1}$ H} NMR spectra were referenced to internal C<sub>6</sub>D<sub>5</sub>H ( $^{1}$ H,  $\delta$ 7.154;  ${}^{13}C$ ,  $\delta$  128.0) and THF- $d_8$  (<sup>1</sup>H,  $\delta$  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 to 80 °C for 3 days. The resulting solution was concentrated under vacuum and stored at -30 °C. Colorless crystals of 1–3 were formed within 12 h.

[MeZnOC(Me)N-*i*-Pr]<sub>4</sub> (1). Yield: 3.43 g (95%). Melting point: 184 °C. Anal. Found (calcd) for  $C_{24}H_{52}N_4O_4Zn_4$  (722.18 g/mol): H, 7.3 (7.3); C, 39.9 (39.9); N, 7.8 (7.8). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –0.36 (s, 3H, Zn*CH*<sub>3</sub>), 1.51 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.71 (s, 3H, CH<sub>3</sub>), 3.18 (sept, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz,

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Table 1.	Crystallographic	c Details for	<b>Complexes 1</b>	. 2. and 5
				-, -,

	1	2	5
empirical formula	$C_{24}H_{52}N_4O_4Zn_4$	$C_{21}H_{45}N_3O_3Zn_3$	C <sub>56</sub> H <sub>88</sub> N <sub>4</sub> O <sub>4</sub> Zn <sub>2</sub> x 0.5 C <sub>12</sub> H <sub>18</sub>
mol wt	722.18	583.71	1093.18
cryst syst	triclinic	triclinic	triclinic
space group	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
$\hat{T}(\mathbf{K})$	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)
$\alpha$ (deg)	74.605(2)	75.062(2)	79.754(3)
$\beta$ (deg)	82.448(2)	76.264(2)	86.258(3)
$\gamma$ (deg)	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
$\mu (\mathrm{mm}^{-1})$	2.876	2.477	0.801
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.440	1.333	1.145
cryst dimens (mm)	0.36  imes 0.32  imes 0.25	0.36  imes 0.32  imes 0.26	0.28  imes 0.24  imes 0.17
no. of rflns	22 481	17 582	29 180
no. of unique rflns	8223	5350	14 253
R <sub>merg</sub>	0.0225	0.0190	0.0175
no. of params refined/restraints	325/0	271/0	631/0
R1 <sup>a</sup>	0.0197	0.0283	0.0375
$wR2^b$	0.0515	0.0767	0.1068
goodness of fit <sup>c</sup>	1.085	1.059	1.016
final max/min $\Delta \rho$ (e Å <sup>-3</sup> )	0.484/-0.454	0.510/-0.258	0.632/-0.498

 ${}^{a}\mathbf{R}1 = \sum(||F_{o}| - |F_{c}||)/\sum|F_{o}| \text{ (for } I > 2\sigma(I)). - {}^{b}\mathbf{w}\mathbf{R}2 = \{\sum[w(F_{o}^{2} - F_{c}^{2})^{2}]/\sum[w(F_{o}^{2})^{2}]\}^{1/2} \text{ (for all data). } {}^{c}\mathbf{Goodness of fit} = \{\sum[w(|F_{o}^{2}| - |F_{c}^{2}|)^{2}]/(N_{observns} - N_{params})\}^{1/2}.$ 

		0	
Table 2. Selected	Bond Lengths (A	A) and Angles	(deg) of 1 and 2

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

1H, C*H*(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –12.3 (ZnCH<sub>3</sub>), 20.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (CH<sub>3</sub>), 50.0 (CH(CH<sub>3</sub>)<sub>2</sub>), 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 cm<sup>-1</sup>.

[MeZnOC(Me)N-*t*-Bu]<sub>3</sub> (2). Yield: 2.66 g (91%). Melting point: 188 °C. Anal. Found (calcd) for C<sub>21</sub>H<sub>45</sub>N<sub>3</sub>O<sub>3</sub>Zn<sub>3</sub> (583.71 g/mol): H, 7.8 (7.8); C, 43.1 (43.2); N, 7.1 (7.2). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  −0.26 (s, 3H, ZnCH<sub>3</sub>), 1.08 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.89 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  −14.3 (ZnCH<sub>3</sub>), 20.5 (CH<sub>3</sub>), 30.9 (C(CH<sub>3</sub>)<sub>3</sub>), 50.6 (C(CH<sub>3</sub>)<sub>3</sub>), 173.6 (NCO). IR:  $\nu$  2974, 2901, 2832, 1572, 1466, 1381, 1363, 1339, 1214, 1162, 1154, 1064, 1033, 999, 846, 788, 667, 615, 594, 573, 530, 489, 407 cm<sup>-1</sup>.

 $[{MeZn}_4Zn{OC(Me)NC_6F_5}_6]$  (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 to 80 °C for 3 days. The suspension was filtered, and the resulting solid was recrystallized from a solution

in CH<sub>2</sub>Cl<sub>2</sub> 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  $C_{53}H_{33}N_6F_{30}O_6Zn_5$  (1746.69 g/mol): H, 2.0 (1.9); C, 36.4 (36.4); N, 4.9 (4.8). <sup>1</sup>H NMR (300 MHz, THF- $d_8$ , 25 °C):  $\delta$  -0.94 (s, 12H, ZnCH<sub>3</sub>), 1.81 (s, 6H, CH<sub>3</sub>), 2.11 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz,  $C_6D_6$ , 25 °C):  $\delta$  1.4 (ZnCH<sub>3</sub>), 21.0 (CH<sub>3</sub>), 137.1 (Ar C), 140.5 (Ar C), 141.9 (Ar C), 145.2 (Ar C), 182.3 (NCO). <sup>19</sup>F NMR (300 MHz,  $C_6D_6$ , 25 °C): -147.1, -149.0, -162.8, -164.3, -165.6. IR:  $\nu$  2963, 1573, 1504, 1410, 1259, 1085, 1020, 989, 88, 792, 712, 656, 539, 505, 399 cm<sup>-1</sup>.

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 to 60 °C for 3 h. The resulting solution was concentrated under vacuum and stored at 0 °C. Colorless crystalline solids of 4–6 were formed within 12 h.

[**Zn**{**OC**(**Cp**<sup>\*</sup>)**NEt**}<sub>2</sub>]<sub>2</sub>(4). Yield: 0.43 g (89%). Melting point: 257 °C. Anal. Found (calcd) for  $C_{52}H_{80}N_4O_4Zn_2$  (955.98 g/mol): H, 8.4 (8.4); C, 64.4 (65.3); N, 5.4 (5.9). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.15 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.58 (s, 3H, C<sub>5</sub>Me<sub>5</sub>), 1.68 (s, 6H, C<sub>5</sub>Me<sub>5</sub>), 1.96 (s, 6H, C<sub>5</sub>Me<sub>5</sub>), 2.95 (q, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  10.3 (C<sub>5</sub>Me<sub>5</sub>), 11.2 (C<sub>5</sub>Me<sub>5</sub>), 18.2 (C<sub>5</sub>Me<sub>5</sub>), 23.2 (CH<sub>3</sub>), 34.2 (CH<sub>2</sub>), 65.6 (C<sub>5</sub>Me<sub>5</sub>), 136.3 (C<sub>5</sub>Me<sub>5</sub>), 140.1 (C<sub>5</sub>Me<sub>5</sub>), 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<sup>-1</sup>.

[**Zn**{**OC**(**Cp**<sup>\*</sup>)**N**-*i*-**Pr**}<sub>**2**]<sub>**2**</sub></sub> (**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). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  1.18 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.2 Hz, 6H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 1.60 (s, 3H, *C*<sub>5</sub>*Me*<sub>5</sub>), 1.69 (s, 6H, *C*<sub>5</sub>*Me*<sub>5</sub>), 1.99 (s, 6H, *C*<sub>5</sub>*Me*<sub>5</sub>), 3.41 (sept, <sup>3</sup>*J*<sub>HH</sub> = 6.0 Hz, 1H, *CH*(*CH*<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  10.2 (*C*<sub>5</sub>*Me*<sub>5</sub>), 11.00 (*C*<sub>5</sub>*Me*<sub>5</sub>), 23.8 (*C*<sub>5</sub>*Me*<sub>5</sub>), 26.4 (*CH*<sub>3</sub>), 49.9 (*CH*), 66.1 (*C*<sub>5</sub>*Me*<sub>5</sub>), 135.3 (*C*<sub>5</sub>*Me*<sub>5</sub>), 140.1 (*C*<sub>5</sub>*Me*<sub>5</sub>), 175.4 (NCO). IR: *v* 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<sup>-1</sup>.

[**Zn**{SC(**Cp**\*)**N**-*i*-**Pr**}<sub>2</sub>]<sub>2</sub> (6). Yield: 0.34 g (63%). Melting point: 189 °C. Anal. Found (calcd) for C<sub>56</sub>H<sub>88</sub>N<sub>4</sub>S<sub>4</sub>Zn<sub>2</sub> (1076.33 g/mol): H, 8.1 (8.2); C, 60.2 (62.5); N, 4.8 (5.2); S 10.4 (11.9). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  0.85 (d, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.36 (s, 3H, C<sub>5</sub>Me<sub>5</sub>), 1.74 (s, 6H, C<sub>5</sub>Me<sub>5</sub>), 1.82 (s, 6H, C<sub>5</sub>Me<sub>5</sub>), 3.21 (sept, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 1H, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  10.6 (C<sub>5</sub>Me<sub>5</sub>), 11.1 (C<sub>5</sub>Me<sub>5</sub>), 24.1 (C<sub>5</sub>Me<sub>5</sub>), 26.9 (CH<sub>3</sub>), 50.1 (CH), 66.2 (C<sub>5</sub>Me<sub>5</sub>), 135.6 (C<sub>5</sub>Me<sub>5</sub>), 140.8 (C<sub>5</sub>Me<sub>5</sub>), 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<sup>-1</sup>.

Single-Crystal X-ray Analyses. Crystallographic data for 1, 2, and 5, which were collected on a Bruker AXS D8 Kappa diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å), are summarized in Table 1; selected bond lengths and angles are given 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)<sup>25</sup> and refined anisotropically by full-matrix least squares on  $F^2$  (SHELXL-97).<sup>26</sup> Absorption

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Table 3. Selected Bond Lengths (Å) and Angles (deg) of 5

		8 ( ) 8	
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)

corrections were performed semiempirically from equivalent reflections on the basis of multiscans (Buker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The poor quality of the crystal of  $3 (\theta_{max} = 23^{\circ})$  prevented a proper refinement of the structure model (R1 above 0.15, no anisotropic refinement possible). However, the connectivity and atom types were determined without doubt. **5** crystallizes with one molecule of diisopropylbenzene disordered over a center of inversion. The corrosponding carbon atoms were refined isotropically, and the phenyl ring was constrained 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 nos. 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, U.K. (fax, int.code\_(1223)336-033; e-mail for inquiry, fileserv@ccdc.cam.ac.uk; e-mail for deposition, deposit@ccdc.cam.ac.uk).

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**Supporting Information Available:** CIF files giving crystallographic data for complexes **1**, **2**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.