# Syntheses and X-Ray Structures of Zinc Amidinate Complexes

Tamara Eisenmann, Jayaprakash Khanderi, Stephan Schulz\*, and Ulrich Flörke

Paderborn, Universität, Chemistry Department

Received August 16th, 2007.

Abstract. Reactions of  $ZnX_2$  (X = Cl, Br) with equimolar amounts of Li[*t*-BuC(NR)<sub>2</sub>] (R = *i*-Pr, Cy) yielded mono-amidinate complexes [{*t*-BuC(NR)<sub>2</sub>}ZnX]<sub>2</sub> (X = Cl, R = *i*-Pr 1, Cy 2; X = Br, R = *i*-Pr 3, Cy 4), whereas reactions with two equivalents of Li-amidinate resulted in the formation of the corresponding bis-amidinate complexes [*t*-BuC(NR)<sub>2</sub>]<sub>2</sub>Zn (R = *i*-Pr 5, Cy 6). 1 - 6 were characterized by elemental analyses, IR, mass and multinuclear NMR spectroscopy

# Introduction

*N*,*N*'-chelating organic ligands have attracted growing interest in organometallic chemistry in the last decade and several systems including  $\beta$ -diketiminate I [1], guanidinate II [2], and amidinate anions III [3], have been investigated intensely in both main group and transition metal chemistry [4]. Steric and electronic properties of these *N*,*N*'-chelating substituents can simply be modified by use of different organic substituents R and R', allowing fine-tuning of the chemical properties of the resulting metal complexes. Consequently, a large variety of unforeseen low-coordinate organometallic compounds in low oxidation states have been synthesized and structurally characterized.



 $\mathbf{R}, \mathbf{R} = aikyi, aryi, 5ime_3$ 

Scheme 1 Typical N,N' chelating ligands:  $\beta$ -diketiminate I, guanidinate II and amidinate anions III.

In case of organozinc chemistry, the interest has focused on  $\beta$ -diketiminato complexes of the general type LZnR (L =  $\beta$ -diketiminate) [5], which were shown to be active catalysts in the metal catalyzed ring-opening polymerization (ROP) of cyclic esters, in particular lactides [6], and in (<sup>1</sup>H, <sup>13</sup>C), and single crystal X-ray analysis (1, 2, 3, 6). In addition, the single crystal X-ray structure of  $[t-BuC(NCy)_2]ZnBr\cdotLiBr(OEt_2)_2$  7, which was obtained as a byproduct in low yield from re-crystallization experiments of 4 in Et<sub>2</sub>O, is reported.

Keywords: Zinc; Amides; Bridging Ligands; Coordination Modes; X-Ray Structures

copolymerization of CO<sub>2</sub> and epoxides, respectively [7]. Moreover, low-valent organozinc compounds of the general type LZn-ZnL containing a direct Zn-Zn bond, which were initially prepared by Carmona et al. [8], can be stabilized by use of chelating organic substituents. (L =  $[\{(2,6-i-Pr_2C_6H_3)N(Me)C\}_2CH]$  [9], 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene [10]). Surprisingly, zinc guanidinate and amidinate complexes have been studied to a far lesser extend, which is in remarkable contrast to well known beryllium [11] and magnesium complexes [12]. Coles et al. reported on the synthesis of a very few guanidinate complexes and their application in ROP catalysis [13], whereas, to the best of our knowledge, zinc amidinate complexes haven't been structurally characterized except for a very few formamidinate complexes [14]. In addition, Edelmann et al. described the synthesis of a bis-benzamidinate zinc complex [15] and very recently, Chivers et al. reported on the synthesis and X-ray crystal structure of bis-boraamidinate zinc complexes [16].

Herein, we report on the synthesis and single crystal Xray structures of mono- and bis-amidinate zinc complexes, which were obtained from reactions of zinc halides  $ZnX_2$ (X = Cl, Br) with either one or two equivalents of the corresponding Li-amidinate Li[*t*-BuC(NR)<sub>2</sub>] (R = *i*-Pr, Cy).

# **Experimental Section**

# **General Procedure**

All manipulations were performed in a glovebox under an N<sub>2</sub> atmosphere or with standard Schlenk techniques. Solvents were dried over sodium/potassium or by use of a solvent purification system (MBRAUN) and degassed prior to use. Li-amidinates Li[*t*-BuC(NR)<sub>2</sub>] (R = *i*-Pr, Cy) were prepared by reaction of *t*-BuLi with the corresponding carbodiimide RN=C=NR according to a procedure described by *Jordan* et al. [17]. A Bruker Avance 500 spectrometer was used for NMR spectroscopy. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to internal C<sub>6</sub>D<sub>5</sub>H (<sup>1</sup>H:  $\delta$  = 7.154;



<sup>\*</sup> Prof. Dr. Stephan Schulz Anorganische Chemie Universitätsstrasse 5–7 Raum S05 T05 B84 Universität Duisburg-Essen 45117 Essen Fax: 0201/1833830 E-mail: stephan.schulz@uni-due.de

<sup>13</sup>C:  $\delta = 128.0$ ) and THF-d<sub>8</sub> (<sup>1</sup>H:  $\delta = 1.73$ ; 3.58; <sup>13</sup>C:  $\delta = 25.2$ ; 67.4). Mass spectra (EI) were recorded on a Finnigan MAT 8230 spectrometer. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Paderborn.

General Synthesis of [{*t*-BuC(NR)<sub>2</sub>}ZnX]<sub>2</sub> (X = Cl, Br; R = *i*-Pr, Cy): 5 mmol Li[*t*-BuC(NR)<sub>2</sub>] (R = *i*-Pr 0.951 g; Cy 1.352 g) dissolved in 30 mL of Et<sub>2</sub>O was slowly added at -78 °C to a suspension of 5 mmol ZnX<sub>2</sub> (X = Cl 0.681 g; Br 1.125 g) in 40 mL Et<sub>2</sub>O and stirred for 1h. After warming up to room temperature the reaction mixture was allowed to stir additional 12h. Et<sub>2</sub>O was removed at reduced pressure and the remaining yellowish solid was suspended in 30 mL of *E*t<sub>2</sub>O, filtered and then the Et<sub>2</sub>O removed at reduced pressure. The resulting solid was re-crystallized from solutions in toluene / Et<sub>2</sub>O at -30 °C, yielding colorless crystals of 1 - 4. Yields are given for the isolated crystalline materials.

 ${t-BuC(Ni-Pr)_2}ZnCl]_2$  1: Yield 0.78 g (55 %). Mp: > 220 °C. Anal. C<sub>22</sub>H<sub>46</sub>Cl<sub>2</sub>N<sub>4</sub>Zn<sub>2</sub> (568.28 g/mol): found (calcd): H, 8.11 (8.16); C: 46.23 (46.50) %.

<sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.01 (d, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 12H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 1.36 (s, 9H, *t*-Bu), 4.11 (sep, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 2H, *CH*(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C): δ 27.8 (CH*Me*<sub>2</sub>); 30.5 (CC*Me*<sub>3</sub>), 40.0 (CCMe<sub>3</sub>), 46.5 (CHMe<sub>2</sub>), 176.3 (CCMe<sub>3</sub>). **EI-MS** (70 eV, 150 °C): *m/z* (%): 43 (100) [*i*-Pr]<sup>+</sup>, 57 (70) [*t*-Bu]<sup>+</sup>, 84 (90) [*t*-BuC(N*i*-Pr)<sub>2</sub>-*t*-Bu<sup>-*i*</sup>-Pr]<sup>+</sup>, 183 (100) [*t*-BuC(N*i*-Pr)<sub>2</sub>]<sup>+</sup>, 282 (5) [*M*/2]<sup>+</sup>. **IR** (nujol): v 2916, 2717, 1460, 1378, 1259, 1087, 1026, 881, 798, 731 cm<sup>-1</sup>.

 ${t-BuC(NCy)_2}ZnCl_2 2$ : Yield 0.64 g (42 %). Mp: > 220 °C. Anal. C<sub>34</sub>H<sub>62</sub>Cl<sub>2</sub>N<sub>4</sub>Zn<sub>2</sub> (728,54 g/mol): found (calcd): H, 8.43 (8.58); C: 55.78 (56.05) %.

<sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  1.08–1.14 (m, 4H, CH<sub>2</sub>), 1.26–1.37 (m, 8H, CH<sub>2</sub>), 1.36 (s, 9H, *t*-Bu), 1.68–1.74 (m, 4H, CH<sub>2</sub>), 1.75–1.84 (m, 4H, CH<sub>2</sub>), 3.21–3.33 (m, 2H, CH). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C):  $\delta$  26.4 (C3/C5); 26.7 (C4), 30.5 (CMe<sub>3</sub>), 38.7 (C2/C6), 49.9 (CMe<sub>3</sub>), 55.1 (N-C1), 176.4 (CCMe<sub>3</sub>). EI-MS (70 eV, 150 °C): *m/z* (%): 43 (85) [*t*-Bu-Me]<sup>+</sup>, 57 (90) [*t*-Bu]<sup>+</sup>, 84 (100) [CyH]<sup>+</sup>, 109 (65) [CyNC]<sup>+</sup>, 166 (90) [*t*-BuC(NCy)]<sup>+</sup>, 181 (90) [*t*-BuC(NCy)<sub>2</sub>-Cy]<sup>+</sup>, 263 (95) [*t*-BuC(NCy)<sub>2</sub>]<sup>+</sup>, 327 (10) [M/ 2–CI]<sup>+</sup>, 362 (15) [M/2]<sup>+</sup>. **IR** (nujol): v 2717, 2360, 1465, 1372, 1263, 1087, 1015, 793, 720 cm<sup>-1</sup>.

 $\{t-BuC(Ni-Pr)_2\}ZnBr]_2$  3: Yield 0.78 g (35 %) Mp: > 220 °C. Anal. C<sub>22</sub>H<sub>46</sub>Br<sub>2</sub>N<sub>4</sub>Zn<sub>2</sub> (657.18 g/mol): found (calcd): H, 6.98 (7.05); C: 40.11 (40.21) %.

<sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.02 (d,  ${}^{3}J_{HH} = 6.1$  Hz, 12H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 1.38 (s, 9H, *t*-Bu), 4.16 (sep,  ${}^{3}J_{HH} = 6.1$  Hz, 2H, *CH*(CH<sub>3</sub>)<sub>2</sub>).  ${}^{12}C$  NMR (125 MHz, THF-d<sub>8</sub>, 25 °C): δ 27.3 (CH*Me*<sub>2</sub>); 30.4 (CC*Me*<sub>3</sub>), 40.1 (CCMe<sub>3</sub>), 46.7 (CHMe<sub>2</sub>), 176.4 (CCMe<sub>3</sub>). EI-MS (70 eV, 150 °C): *mlz* (%): 43 (80) [*i*-Pr]<sup>+</sup>, 58 (90) [*t*-BuH]<sup>+</sup>, 83 (100) [*t*-BuC(N*i*-Pr)<sub>2</sub>-*t*-Bu-*i*-Pr]<sup>+</sup>, 126 (40) [*t*-BuC(N*i*-Pr)<sub>2</sub>]<sup>+</sup>, 247 (10) [M/2-Br]<sup>+</sup>, 328 (15) [M/2]<sup>+</sup>. IR (nujol): v 2955, 2918, 2852, 1646, 1563, 1465, 1374, 1263, 1155, 1103, 1015, 818 cm<sup>-1</sup>.

 ${t-BuC(NCy)_2}ZnBr]_2 4$ : Yield 1.13 g (46 %). Mp: > 220 °C. Anal. C<sub>34</sub>H<sub>62</sub>Br<sub>2</sub>N<sub>4</sub>Zn<sub>2</sub> (817.44 g/mol): found (calcd): H, 7.55 (7.64); C: 49.77 (49.96) %.

<sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.02-1.16 (m, 2H + 4H), 1.20-1.31 (m (br), 2H + 4H, CH<sub>2</sub>), 1.34 (s, 9H, *t*-Bu), 1.51-1.59 (m (br), 2H, CH<sub>2</sub>), 1.63–1.71 (m (br), 4H, CH<sub>2</sub>), 1.75–1.80 (m (br), 2H, CH<sub>2</sub>), 3.62 (m, 2H, CH<sub>2</sub>), <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C): δ 26.7 (C3/C5); 26.9 (C4), 30.6 (CMe<sub>3</sub>), 38.5 (C2/C6), 40.1 (CMe<sub>3</sub>), 55.7 (N-C1), 176.5 (CCMe<sub>3</sub>). **EI-MS** (70 eV, 150 °C): m/z (%): 43 (75) [*t*-Bu-Me]<sup>+</sup>, 57 (100) [*t*-Bu]<sup>+</sup>, 84 (90) [CyH]<sup>+</sup>, 109 (35) [CyNC]<sup>+</sup>, 166 (55) [*t*-BuC(NCy)]<sup>+</sup>, 181 (95) [*t*-BuC(NCy)<sub>2</sub>-*c*y]<sup>+</sup>, 206 (25) [*t*-BuC(NCy)<sub>2</sub>-*t*-Bu]<sup>+</sup>, 263 (85) [*t*-BuC(NCy)<sub>2</sub>]<sup>+</sup>, 327 (5) [M/2-Br]<sup>+</sup>, 408 (3) [M/2]<sup>+</sup>. **IR** (nujol): v 2717, 1620, 460, 1372, 1264, 1093, 865, 803 cm<sup>-1</sup>.

**General Synthesis of** [*t***-BuC(NR)**<sub>2</sub>]<sub>2</sub>**Zn** (**R** = *i*-**Pr**, **Cy**): 5 mmol Li[*t*-BuC(NR)<sub>2</sub>] (**R** = *i*-**Pr** 0.951 g; Cy 1.352 g) dissolved in 30 mL of Et<sub>2</sub>O was slowly added at -78 °C to a suspension of 2.5 mmol ZnX<sub>2</sub> (**X** = Cl 0.341; Br 0.562 g) in 40 mL of Et<sub>2</sub>O. The resulting suspension was warmed up to ambient temperature and stirred for 12h. Thereafter, Et<sub>2</sub>O was distilled of and the remaining solid suspended in *n*-hexane. Filtration yielded a clear solution, which was concentrated to 5 mL and stored at -30 °C. Colorless crystals were formed within 24h. Yields are given for the crystalline complexes.

 $[t-BuC(Ni-Pr)_2]_2Zn 5$ : Yield 0.85 g (80 %). Mp: > 220 °C. Anal. C<sub>22</sub>H<sub>46</sub>N<sub>4</sub>Zn (432.00 g/mol): found (calcd): H, 10.71 (10.73); C: 61.13 (61.17) %.

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 12H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 1.31 (s, 9H, *t*-Bu), 4.16 (sep, <sup>3</sup>J<sub>HH</sub> = 5.9 Hz, 2H, *CH*(CH<sub>3</sub>)<sub>2</sub>). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.03 (d, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 12H, CH(*CH*<sub>3</sub>)<sub>2</sub>), 1.40 (s, 9H, *t*-Bu), 4.14 (sep, <sup>3</sup>J<sub>HH</sub> = 6.1 Hz, 2H, *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): δ 27.6 (CH*M*e<sub>2</sub>); 30.3 (CC*M*e<sub>3</sub>), 39.5 (CCMe<sub>3</sub>), 46.0 (CHMe<sub>2</sub>), 175.9 (CCMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 27.6 (CH*M*e<sub>2</sub>); 30.3 (CC*M*e<sub>3</sub>), 39.5 (CCMe<sub>3</sub>), 46.0 (CHMe<sub>2</sub>), 175.9 (CCMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C): δ 27.8 (CH*M*e<sub>2</sub>); 30.6 (CC*M*e<sub>3</sub>), 40.1 (CCMe<sub>3</sub>), 46.5 (CHMe<sub>2</sub>), 176.4 (CCMe<sub>3</sub>). EL-MS (70 eV, 100 °C): *m*/z (%): 43 (90) [*i*-Pr]<sup>+</sup>, 57 (90) [*t*-Bu]<sup>+</sup>, 183 (100) [*t*-BuC(N*i*-Pr)<sub>2</sub>–*t*-Bu–*i*-Pr]<sup>+</sup>, 126 (90) [*t*-BuC(N*i*-Pr)<sub>2</sub>–*t*-Bu]<sup>+</sup>, 183 (100) [*t*-BuC(N*i*-Pr)<sub>2</sub><sup>+</sup>, 388 (80) [M–*t*-Pr]<sup>+</sup>, 430 (80) [M]<sup>+</sup>. **IR** (nujol): v 2960, 2924, 2857, 1455, 1424, 1378, 1316, 1264, 1186, 1119, 1041, 866, 793 cm<sup>-1</sup>.

 $[t-BuC(NCy)_2]_2Zn$  6: Yield 1.30 g (83 %). Mp: > 220 °C. Anal. C<sub>34</sub>H<sub>62</sub>N<sub>4</sub>Zn (592.26 g/mol): found (calcd): H, 10.52 (10.55); C: 68.73 (68.95).

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 1.09-1.19 (m, 2H, H(4)<sub>ax</sub>), 1.23–1.36 (m, 4H, H(3/5)<sub>ax</sub>), 1.37 (s, 9H, *t*-Bu), 1.38–1.49 (m, 4H, H(2/6)<sub>ax</sub>), 1.57 (d (br), 2H, H(4)<sub>eq</sub>), 1.76 (d (br), 4H, H(3/5)<sub>eq</sub>), 2.04 (d (br), 4H, H(2/6)<sub>eq</sub>), 3.77 (tt, <sup>3</sup>J<sub>HH</sub> = 10.1 Hz, <sup>3</sup>J<sub>HH</sub> = 3.8 Hz, 2H, H(1)<sub>ax</sub>). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.06-1.15 (m, 2H + 4H, H(4)<sub>ax</sub> + H(3/5)<sub>ax</sub>), 1.23-1.30 (m, 4H, H(2/6)<sub>ex</sub>), 1.38 (s, 9H, *t*-Bu), 1.58 (d (br), 2H, H(4)<sub>eq</sub>), 1.69 (d (br), 4H, H(3/5)<sub>eq</sub>), 1.78 (d (br), 4H, H(2/6)<sub>eq</sub>), 3.60 (tt, <sup>3</sup>J<sub>HH</sub> = 10.2 Hz, <sup>3</sup>J<sub>HH</sub> = 3.8 Hz, 2H, H(1)<sub>ax</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 26.1 (C3/C5); 26.3 (C4), 30.4 (CMe<sub>3</sub>), 38.7 (C2/C6), 39.5 (CMe<sub>3</sub>), 54.9 (N-C1), 176.2 (CCMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C): δ 26.5 (C3/C5); 26.9 (C4), 30.6 (CMe<sub>3</sub>), 39.1 (C2/C6), 40.0 (CMe<sub>3</sub>), 55.3 (N-C1), 176.5 (CCMe<sub>3</sub>). EI-MS (70 eV, 100 °C): *m/z* (%): 57 (45) [*t*-Bu<sup>+</sup>, 84 (100) [CyH]<sup>+</sup>, 181 (30) [*t*-BuC(NCy)<sub>2</sub>-Cy]<sup>+</sup>, 263 (100) [*t*-BuC(NCy)<sub>2</sub>]<sup>+</sup>, 327 (20) [*t*-BuC(N*i*-Pr)<sub>2</sub>Zn]<sup>+</sup>, 507 (20) [(M-Cy])<sup>+</sup>, 590 (15) [M]<sup>+</sup>. IR (nujol): v 2956, 2842, 2733, 2668, 1651, 1460, 1379, 1341, 1297, 1172, 1129, 884 cm<sup>-1</sup>.

#### [t-BuC(NCy)<sub>2</sub>ZnBr x LiBr(OEt<sub>2</sub>)<sub>2</sub>] 7:

<sup>1</sup>**H** NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ 1.06-1.15 (m, 4H, Cy), 1.12 (t,  ${}^{3}J_{HH} = 6.9$  Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.20-1.29 (m, 8H, Cy), 1.34 (s, 9H, *t*-Bu), 1.55 (m, 2H, Cy), 1.66 (m, 4H, Cy), 1.77 (m, 2H, Cy), 3.39 (q,  ${}^{3}J_{HH} = 6.9$  Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 3.58 (m, 2H, Cy). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C): δ 15.7 (OCH<sub>2</sub>CH<sub>3</sub>), 26.4 (C3/C5); 26.8 (C4), 30.6 (CMe<sub>3</sub>), 38.5 (C2/C6), 39.1 (CMe<sub>3</sub>), 55.6 (N-C1), 66.3 (OCH<sub>2</sub>CH<sub>3</sub>), 176.5 (CCMe<sub>3</sub>). **EI-MS** (70 eV, 150 °C): m/z (%): 29 (15) [Et]<sup>+</sup>, 57 (60) [*t*-Bu]<sup>+</sup>, 84 (100) [CyH]<sup>+</sup>, 98 (50) [NCyH]<sup>+</sup>, 167 (30) [*t*-BuC(NCy)H]<sup>+</sup>, 181 (90) [*t*-BuC(NCy)<sub>2</sub>-Cy]<sup>+</sup>, 264 (65) [*t*-BuC(NCy)<sub>2</sub>H]<sup>+</sup>. **IR** (nujol): v 2960, 2846, 2670, 1460, 1372, 1258, 1087, 1025, 798 cm<sup>-1</sup>.

### X-ray Structure Solution and Refinement

Bond lengths and angles for 1, 2, 3, 6 and 7 are summarized in Table 1. Crystallographic data of 1, 2 and 3 are given in Table 2, those of 6 and 7 in Table 3. Figures 2-5 show ORTEP diagrams of the solid state structures of 2, 3, 6 and 7. Data were collected on a Bruker-AXS SMART APEX CCD. The structures were solved by Direct Methods (SHELXS-97) [18] and refined by full-matrix leastsquares on F<sup>2</sup> (SHELXL-97) [19]. Multi-scan absorption corrections were applied for 1, 2, 3, 6 and 7. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. The crystallographic data of 1, 2, 3, 6 and 7 (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-648547 (1), CCDC-644935 (2), CCDC-646888 (3), CCDC-644934 (6), CCDC-644936 (7). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (Telefax: (+44) 1223/336033; E-mail: deposit@ccdc.cam-ak.uk).

**Table 1**Crystallographic details for 1, 2 and 3.

	1	2	3
empirical formula	C22H46Cl2N4Zn2	C41H70Cl2N4Zn2	$C_{22}H_{46}Br_2N_4Zn_2$
molecular mass	568.27	820.65	657.19
cryst syst	monoclinic	monoclinic	monoclinic
space group	P2 <sub>1</sub> /n (no.14)	$P2_1/c$ (no.14)	P2 <sub>1</sub> /n (no.14)
a /Å	9.4749(11)	12.2207(15)	9.6188(12)
b/Å	10.5814(12)	17.269(2)	10.6682(13)
c /Á	13.3037(15)	10.2976(13)	13.4013(16)
β/deg	92.461(2)	104.425(3)	91.751(3)
$V/Å^3$	1332.6(3)	2104.7(5)	1374.5(3)
Ζ	2	2	2
T/K	120(2)	120(2)	120(2)
radiation (λ/Å)	Mo- $K_{\alpha}(0.71073)$	Mo- $K_{\alpha}$ (0.71073)	Mo- $K_{\alpha}$ (0.71073)
$\mu$ /mm <sup>-1</sup>	2.017	1.299	4.668
$D_{calcd.}/g cm^{-3}$	1.416	1.295	1.588
$2\theta_{\rm max}$ /deg	56	56	56
cryst dimens. /mm	0.42 x 0.41 x 0.33	0.26 x 0.20 x 0.13	0.28 x 0.22 x 0.21
no. of reflns	11465	18369	11783
no. of unique reflns	3171	5013	3268
R <sub>merg</sub>	0.0245	0.0452	0.0397
no. of param.	136/0	235/0	136/0
refined/restraints			
$R1^{\rm a}$	0.0245	0.0429	0.0284
wR2 <sup>b</sup>	0.0634	0.1062	0.0684
goodness of fit <sup>c</sup>	1.035	1.100	1.033
final max/min. $\Delta \rho$ , e Å <sup>-3</sup>	0.477 / -0.300	0.783 / -0.295	0.769/-0.381

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

Table 2Crystallographic details for 6 and 7.

	6	7
empirical formula	C34H62N4Zn	C <sub>25</sub> H <sub>51</sub> Br <sub>2</sub> LiN <sub>2</sub> O <sub>2</sub> Zn
molecular mass	592.25	643.81
cryst syst	monoclinic	monoclinic
space group	P2 <sub>1</sub> /n (no.14)	P2 <sub>1</sub> /n (no.14)
a /Å	10.961(7)	9.4466(11)
b /Å	17.100(11)	17.505(2)
c /Å	21.196(12)	18.741(2)
β /deg	117.78(3)	94.019(3)
V /Å <sup>3</sup>	3515(4)	3091.4(6)
Ζ	4	4
Т /К	293(2)	120(2)
radiation (λ/Å)	Mo- $K_{\alpha}$ (0.71073)	Mo- $K_{\alpha}$ (0.71073)
$\mu / \text{mm}^{-1}$	0.725	3.401
$D_{calcd}$ /g cm <sup>-3</sup>	1.119	1.383
$2\theta_{\rm max}/{\rm deg}$	56	56
cryst dimens /mm	0.41 x 0.35 x 0.22	0.43 x 0.24 x 0.18
no. of reflns	28357	27008
no. of unique reflns	8352	7357
R <sub>merg</sub>	0.1124	0.0455
no. of param. refined/restraints	352 / 0	298 / 0
R1 <sup>a</sup>	0.0772	0.0333
wR2 <sup>b</sup>	0.2157	0.0803
goodness of fit <sup>c</sup>	1.008	1.006
final max/min. $\Delta \rho$ , e Å <sup>-3</sup>	0.957 / -0.929	0.534 / -0.335

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

## **Results and Discussion**

Equimolar amounts of  $ZnX_2$  (X = Cl, Br) and Li[*t*-BuC-(NR)<sub>2</sub>] (R = *i*-Pr, Cy) dissolved in Et<sub>2</sub>O react at ambient temperature with elimination of LiX and subsequent formation of mono-amidinate complexes [ $\{t$ -BuC(NR)<sub>2</sub> $\}ZnCl$ ]<sub>2</sub> (R = *i*-Pr 1, Cy 2) and [*t*-BuC(NR)<sub>2</sub>ZnBr]<sub>2</sub> (R = *i*-Pr 3, Cy 4). Reactions of ZnCl<sub>2</sub> with two equivalents Li-amidinate yielded [*t*-BuC(NR)<sub>2</sub>]<sub>2</sub>Zn (R = *i*-Pr 5, Cy 6). Pure 1-6 were obtained after re-crystallization from solutions in Et<sub>2</sub>O/toluene (1-4) and hexane (5, 6), respectively, at -30 °C as colorless crystalline solids. In addition, [*t*-BuC(NCy)<sub>2</sub>]ZnBr·LiBr(OEt<sub>2</sub>)<sub>2</sub> 7 was obtained as a byproduct in low yield from re-crystallization experiments of 4 in Et<sub>2</sub>O.



Scheme 2 Synthesis of Zn-amidinate complexes 1 - 6.

Mass spectra of 1-4 show the monomeric unit of the complexes  $(M/2^+)$ , whereas those of 5 and 6 show the molecular ion peak indicating them to be stable under these specific conditions. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** and **6** in  $C_6D_6$  and THF-d<sub>8</sub> each show one set of resonances for the i-Pr and Cy groups as expected for a Zn complex with distorted tetrahedral environment ( $C_{2\nu}$  symmetry). The Cy group in 6 does not undergo ring inversion reactions in solution as can clearly be seen from the <sup>1</sup>H NMR spectrum. The resonances of the axial H atoms  $(H_{ax})$  are well resolved with large coupling constants to the axial (dihedral angle about 180°) and small coupling constants to the equatorial H atoms (dihedral angle about 60°) of adjacent CH<sub>2</sub> groups. The different coupling constants can clearly be seen for the methine H atom (C1H<sub>ax</sub>; triplet of triplet) showing a significantly smaller (3.8 Hz) coupling constant to the equatorial H atoms than to the axial ones (10.1 Hz) as depicted in figure 1. The equatorial H atoms only show large geminal <sup>2</sup>J<sub>HH</sub> couplings yielding broad doublets with the broadening resulting from small <sup>3</sup>J<sub>HH</sub> couplings to the magnetically non-equivalent axial and equatorial H atoms of the adjacent CH<sub>2</sub> groups (spectrum of higher order). The assignment of the <sup>1</sup>H resonances of 6 is based on HH-COSY and DPFGSE-NOE spectroscopy studies. The <sup>1</sup>H NMR spectra of 1-4 in THF-d<sub>8</sub> also show only one set of resonances due to the organic substituents in the expected ratio despite the non-equivalence of the *i*-Pr and Cy groups bonded to the three- and four-coordinated N atoms.



Figure 1 <sup>1</sup>H NMR spectrum of 6 including the assignment of the proton resonances of the Cy groups.

The solid-state structures of compounds 1, 2, 3 and 6 were determined by single crystal X-ray diffraction. Suitable crystals were obtained from solutions in toluene/Et<sub>2</sub>O (95:5; 1, 2, 3) and Et<sub>2</sub>O (6), respectively, at -30 °C. In addition, very few crystals of 7 were obtained from re-crystallization experiments at -30 °C of a solution of 3 prepared in Et<sub>2</sub>O.

1, 3, 6 and 7 crystallize in the monoclinic space group P(2)1/n, 2 in  $P2_1/c$ . 1–3 are centrosymmetric and form dimeric complexes in the solid state with bridging N-centers and the center of symmetry in the  $Zn_2N_2$  ring. In contrast, the comparable Mg complex [HC(NCy)<sub>2</sub>Mg(thf)( $\mu$ -Cl)<sub>2</sub>( $\mu$ -

0.5thf)]<sub>2</sub> contains chlorine bridges between the two Mg centers [20]. **6** and **7** are monomeric in the solid state with the Lewis acidic Zn atom in **7** coordinated by one additional Br atom and  $[\text{Li}(\text{OEt}_2)_2]^+$  as counter ion as was previously observed in  $[\text{Li}(\text{hf}_2(\mu-\text{Br})_2\text{Zn}\{C(\text{SiMe}_3)(\text{SiMe}_2\text{NPhMe})\}]$ [21] and  $[\text{Li}(\text{OEt}_2)_2(\mu-\text{Cl})_2\text{Zn}\{N(\text{Dipp})C(\text{Me})\}_2\text{CH}]$  [5b]. The Zn atoms in **1**–**7** adopt distorted tetrahedral coordination spheres, the Zn-X bond lengths (X = Cl: 2.205(1) **1**, 2.201(1) **2**; X = Br, 2.339(1) **3** Å) are within typical ranges



**Figure 2** Molecular structure and atom numbering scheme of **2**; thermal ellipsoids are drawn at the 50 % probability level. H atoms have been omitted for clarity.



Figure 3 Molecular structure and atom numbering scheme of 3; thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.



**Figure 4** Molecular structure and atom numbering scheme of **6**; thermal ellipsoids are drawn at the 50 % probability level. H atoms have been omitted for clarity.

of terminal Zn-X bond lengths [22]. The Zn-Br bond lengths in 7 (2.407(1), 2.424(1) Å) are comparable to those in [Li(thf)<sub>2</sub>( $\mu$ -Br)<sub>2</sub>Zn{C(SiMe<sub>3</sub>)(SiMe<sub>2</sub>NPhMe)}] (2.403(1), 2.441(1) Å) [21].

The most remarkable structural difference between 1, 2 and 3 on the one hand and 6 and 7 on the other hand is reflected by the different coordination modes of the amidinate ligand. The N atoms in the bis-amidinate complexes 6 and 7 are threefold coordinated and the Zn-N bond lengths are almost equal (2.020(3), 2.023(3), 2.045(3), 2.054(3) 6; 2.009(2), 2.015(2) Å 7). The sum of the bond angles of the central carbon atom of the amidinate ligand (C1 359.7, C6 359.9 6; 359.9° 7) and of the nitrogen atoms (N1 353.6, N2 359.5; N3 359.7, N4 359.8 6; N1 358.4, N2 359.0° 7) prove the amidinate ligand to be nearly planar with sp<sup>2</sup>-hybridized C and N atoms. Moreover, the almost equal C-

Table 3 Selected bond lengths /Å and angles  $/\circ$  of 1, 2 and 3.

	1	2	3
Zn1-N1 / Zn1-N1A	2.146(2) / 2.038(2)	2.118(2) / 2.049(2)	2.145(2) / 2.039(2)
Zn1-N2	2.078(2)	2.076(2)	2.077(2)
Zn1-X (X = Cl, Br)	2.205(1)	2.201(1)	2.339(1)
Li1-Br1 / Li1-Br2			
1: C7-N1 / C7-N2	1.432(2) / 1.292(2)	1.428(3) / 1.293(3)	1.432(3) / 1.291(3)
2, 3: C1-N1 / C1-N2			
1: N1-C1 / N2-C4	1.499(2) / 1.479(2)	1.500(3) / 1.476(3)	1.495(3) / 1.481(3)
2: N1-C11 / N2-C21			
3: N1-C9 / N2-C6			
N1-Zn1-N2 / N3-Zn1-N4	64.2(1)	69.5(1)	64.4(1)
N1-Zn1-N1A / Zn1-N1-Zn1A	92.2(1) / 87.9(1)	91.2(1) / 88.8(1)	92.5(1) / 87.6(1)
1: N1-C7-N2	111.0(2)	110.6(2)	111.3(2)
2, 3: N1-C1-N2 / N3-C6-N4			
1: C8-C7-N1 / C8-C7-N2	123.1(2) / 125.7(2)	122.7(2) / 126.0(2)	122.9(2) / 125.6(2)
2, 3: C2-C1-N1 / C2-C1-N2			
CX-N1-Zn1 / CY-N2-Zn1	117.6(1) / 136.7(2)	118.9(2) / 136.5(2)	118.2(2) / 136.7(2)
1: $X = 1, Y = 4$			
<b>2</b> : $X = 11, Y = 21$			
<b>3</b> : $X = 9, Y = 6$			



**Figure 5** Molecular structure and atom numbering scheme of 7; thermal ellipsoids are drawn at the 50 % probability level. H atoms have been omitted for clarity.

**Table 4** Selected bond lengths /Å and angles  $/\circ$  of 6 and 7.

	6	7
Zn1-N1 / Zn1-N1A	2.045(3)	2.015(2)
Zn1-N2	2.023(3)	2.009(2)
Zn1-N3 / Zn1-N4	2.020(3) / 2.054(3)	
Zn1-X (X = Cl, Br)		2.424(1) / 2.407(1)
Li1-Br1 / Li1-Br2		2.592(4) / 2.570(4)
C1-N1 / C1-N2	1.349(4) / 1.355(5)	1.342(3) / 1.326(3)
C6-N3 / C6-N4	1.364(5) / 1.338(5)	
N1-C11 / N2-C21	1.480(4) / 1.474(4)	1.459(3) / 1.462(3)
N3-C31 / N4-C41	1.462(5) / 1.476(5)	
N1-Zn1-N2 / N3-Zn1-N4	65.6(2) / 65.7(2)	65.5(1)
N1-Zn1-N3 / N1-Zn1-N4	131.6(2) / 124.9(2)	
N1-C1-N2 / N3-C6-N4	109.2(3) / 109.7(3)	109.2(2)
C2-C1-N1 / C2-C1-N2	126.7(3) / 123.9(3)	122.9(2) / 127.8(2)
C7-C6-N3 / C7-C6-N4	121.2(3) / 121.2(3)	
C11-N1-Zn1 / C21-N2-Zn1	131.6(2) / 135.5(2)	135.4(2) / 132.3(2)

N bond lengths as observed in **6** (C1-N1 1.349(4), C1-N2 1.355(5), C6-N3 1.364(5), C6-N4 1.338(5) Å) and **7** (C1-N1 1.342(3), C1-N2 1.326 (3) Å) are in between typical values for C-N single and C=N double bonds. These structural findings clearly point to an almost perfect delocalization of the  $\pi$ -electrons within the CN<sub>2</sub> backbone of the fourmembered metallacycle.

In sharp contrast, the Zn-N bond lengths in 1, 2 and 3 vary significantly in accordance with the different coordination numbers of the N-atoms (three vs. four). As is expected, the Zn-N bond lengths of the four-coordinate N-atoms (Zn1-N1 2.146(2) 1; 2.118(2) 2; 2.145(2) Å 3) are elongated compared to those of the three-coordinate N-atom (Zn1-N2 2.078(2) 1; 2.076(2) 2; 2.077(2) Å 3). Surprisingly, the Zn1-N1A bond lengths in 1-3 are the shortest ones even though the N atoms are fourfold-coordinate. In addition, the amidinate ligand significantly differs from

planarity as shown by the sum of the bond angles. The three-coordinate carbon and nitrogen atoms in 1 (C7 359.8; N2 359.6°), 2 (C1 359.3; N2 359.9°) and 3 (C1 359.8; N2 359.6°) are almost planar, indicating sp<sup>2</sup>-hybridized centers, whereas significantly smaller sum of bond angles are observed for the four-coordinate nitrogen atoms (N1 319.7 1: 325.5 2; 320.6° 3) [23]. Moreover, the C-N bond lengths within the amidinate moiety of 1 (C7-N1 1.432(2), C7-N2 1.292(2) Å), 2 (C1-N1 1.428(3), C1-N2 1.293(3) Å) and 3 (C1-N1 1.432(3), C1-N2 1.291(3) Å) vary by almost 0.14 Å. clearly revealing the  $\pi$ -electrons to be rather localized at N1. consequently allowing the intermolecular coordination to Zn1A. According to these structural findings, the coordination mode of the amidinate moiety within the complexes 1-3 is better described with the resonance structure **B** (figure 6), whereas that within 6 and 7 better agrees with resonance structure A.



Figure 6 Different resonance structures of the amidinate moieties in complexes 1 - 6.

The almost identical amidinate bite angles (endocyclic N-Zn-N bond angle: 64.2(1) 1; 64.5(1) 2; 64.4(1) 3; 65.6(2), 65.7(2) 6,  $65.5(1)^{\circ}$  7) are within the typical range ( $53.8-84.5^{\circ}$ ) of amidinate complexes containing four-coordinate metal centers (based on 100 entries in the CSD database), but slightly smaller than the mean value of  $68.2^{\circ}$  [24]. The rather acute endocyclic bond angles indicate considerable ring strain to be present in these complexes. Consequently, the exocyclic N1/2-Zn1-X1/2 bond angles (average values: 114.2 1; 113.3 2; 114.1 3; 134.3 6; 121.6^{\circ} 7) are significally widened [25]. In particular the large exocyclic N-Zn-N bond angles in 6 indicates high steric pressure within this bis-amidinate complex. The exocyclic C-N-C and C-C-N bond angles of the amidinate backbones of 1, 2, 3, 6 and 7 are very similar.

# Conclusion

Four mono-amidinate and two bis-amidinate complexes have been prepared by reactions of zinc halides with the corresponding Li-amidinate and characterized by single crystal X-ray analysis. The mono-amidinate complexes, which forms N-bridged dimers in the solid state, may be valuable starting reagents for further substitution reactions (exchange of the halide substituents) as well as for reduction reactions, probably yielding Zn-Zn bonded species. Further investigations are currently in progress. We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (DFG). We also like to thank Dr. Hans Egold, University of Paderborn, for recording COSY and NOE spectra of compound 6.

#### References

- L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* 2002, 102, 3031–3065.
- [2] P. J. Bailey, S. Pace, Coord. Chem. Rev. 2001, 214, 91-141.
- [3] J. Barker, M. Kilner, Coord. Chem. Rev. 1994, 133, 219-300.
- [4] For a very recent perspective article on the use of neutral amidines and guanidines in coordination chemistry see: M. P. Coles, J. Chem. Soc., Dalton Trans. 2006, 985–1001.
- [5] See the following and references cited therein: a) J. Prust, A. Stasch, W. Zheng, H. W. Roesky, E. Alexopoulos, I. Usón, D. Böhler, T. Schuchardt, *Organometallics* 2001, 20, 3825–3828;
  b) J. Prust, H. Hohmeister, A. Stasch, H. W. Roesky, J. Magull, E. Alexopoulos, I. Usón, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* 2002, 2157–2162; c) S. Aboulkacem, W. Tyrra, I. Pantenburg, *Z. Anorg. Allg. Chem.* 2003, 629, 1569–1574.
- [6] a) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 1999, 121, 11583-11584; b) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 2001, 123, 3229-3238; c) M. H. Chisholm, J. C. Huffman, K. Phomphrai, M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, J. Chem. Soc., Dalton Trans. 1999, 222-224; d) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, J. Organomet. Chem. 2003, 683, 137-148; e) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, J. Organomet. Chem. 2003, 683, 137-148; e) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, J. Chem. Soc. 2002, 124, 14284-14285; f) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, Inorg. Chem. 2005, 44, 8004-8010.
- [7] a) S. D. Allen, D. R. Moore, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 2002, 124, 14284–14285; b) B. Y. Liu, C. Y. Tian, L. Zhanq, W. D. Yan, W. J. Zhanq, J. Polym. Sci. Part A: Polym. Chem. 2006, 44, 6243–6251; c) M. Kröger, C. Folli, O. Walter, M. Döring, Adv. Synth. Cat. 2006, 348, 1908–1918; d) M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 2001, 123, 8738–8749.
- [8] a) I. Resa, E. Carmona, E. Gutierrez-Puebla, A. Monge, *Science* 2004, 305, 1136; b) D. del Río, A. Galindo, I. Resa, E. Carmona, *Angew. Chem.* 2005, 117, 1270; *Angew. Chem. Int. Ed.* 2005, 44, 1244–1247.
- Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R.
   B. King, P. v. R. Schleyer, H. F. Schaefer, III, G. H. Robinson, J. Am. Chem. Soc. 2005, 127, 11944–11945.
- [10] I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko,
   A. V. Piskunov, G. H. Fukin, *Angew. Chem.* 2007, 119, 4380–4383; *Angew. Chem. Int. Ed.* 2007, 46, 4302–4305.
- [11] a) B. Neumüller, K. Dehnicke, Z. Anorg. Allg. Chem. 2003, 629, 2529–2534; b) M. Niemeyer, P. P. Power, Inorg. Chem. 1997, 36, 4688–4696.
- [12] See the following and reference cited therein: a) A. R. Sadique, M. J. Heeg, C. H. Winter, *Inorg. Chem.* 2001, 40, 6349–6355;
  b) J. A. R. Schmidt, J. Arnold, J. Chem. Soc., Dalton Trans. 2002, 2890–2899.
- [13] a) M. P. Coles, P. B. Hitchcock, *Eur. J. Inorg. Chem.* 2004, 2662–2672; b) S. J. Birch, S. R. Boss, S. C. Cole, M. P. Coles, R. Haigh, P. B. Hitchcock, A. E. H. Wheatley, *J. Chem. Soc., Dalton Trans.* 2004, 3568–3574.

- [14] a) F. A. Cotton, L. M. Daniels, L. R. Falvello, J. H. Matonic, C. A. Murillo, X. Wang, H. Zhou, *Inorg. Chim. Acta* 1997, 266, 91–102; b) M. L. Cole, D. J. Evans, P. C. Junk, L. M. Louis, *New J. Chem.* 2002, 26, 1015–1024.
- [15] J.-K. Buijink, M. Noltemeyer, F. T. Edelmann, Z. Naturforsch. 1991, 46b, 1328-1332.
- [16] T. Chivers, D. J. Eisler, C. Fedorchuk, G. Schatte, H. M. Tuononen, *Inorg. Chem.* 2006, 45, 2119–2131.
- [17] M. P. Coles, D. C. Swenson, R. F. Jordan, Organometallics 1997, 16, 5183-5194.
- [18] G. M. Sheldrick, SHELXS-97, Program for Structure Solution: Acta Crystallogr. 1990, A46, 467.
- [19] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.
- [20] F. A. Cotton, S. C. Haefner, J. H. Matonic, X. Wang, C. A. Murillo, *Polyhedron* 1997, 16, 541-550.
- [21] D. Azarifar, M. P. Coles, S. M. El-Hamruni, C. Eaborn, P. B. Hitchcock, J. D. Smith, *J. Organomet. Chem.* 2004, 689, 1718–1722.

- [22] Based on more than 1000 entries in the CSD database, terminal Zn-Cl bond lengths of four-coordinated Zn atoms range from 2.068 – 2.416 Å (mean bond length of 2.248 Å), whereas terminal Zn-Br bond lengths range from 2.278 – 2.548 Å (mean bond length of 2.38 Å based on more than 200 entries). Cambridge Structural Database (CSD) Version 5.28, November 2006 including update Mai 2007).
- [23] The sum of bond angles is defined as  $\Sigma$ (C1-N1-C9/11 + C1-N1-Zn1 + C9/11-N1-Zn1.
- [24] 560 amidinate complexes with metal centers in different coordination environments were found in the CSD database. The bite angle ranges from 52 - 86° with a mean value of 62.1°. Cambridge Structural Database (CSD) Version 5.28, November 2006 including update Mai 2007).
- [25] 1: X1 = Cl1, X2 = N1A; 2: X1 = Cl1, X2 = N1A; 3: X1 = Br1, X2 = N1A; 6: X1 = N3, X2 = N4; 7: X1 = Br1, X2 = Br2.