

Synthesis and Structural Characterization of New Zinc Amidinate Complexes

Sarah Schmidt,[†] Stephan Schulz,^{*,†} Dieter Bläser,[†] Roland Boese,[†] and Michael Bolte[‡]

[†]Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany, and [‡]Institute of Inorganic Chemistry, University of Frankfurt, 60438 Frankfurt, Germany

Received September 3, 2010

The synthesis and reactivity of heteroleptic zinc complexes of the type LZnX (X = Me, I) containing amidinate ligands L of varying steric bulk were investigated. Complexes of the type LZnMe, which were obtained from the homoleptic complexes L_2Zn upon reaction with ZnMe₂, react with iodine with subsequent formation of LZnI. Single-crystal X-ray structures of the amidinate zinc complexes [{MeC(N*i*-Pr)₂}ZnMe]₂, 1, [{MeC(N*i*-Pr)₂}ZnI]₂LiI(OEt)₂, 3, [*t*-BuC(NDipp)₂]ZnMe, 5, [*t*-BuC(NDipp)₂]ZnMe(*t*-BuPy), 6, [{*t*-BuC(NDipp)₂}Zn(μ -I)]₂, 7, and [*t*-BuC{N(H)Dipp}₂][Al{OC(CF₃)₃}]₄], 8, are reported.

Introduction

Amidines (LH) and amidinates (L⁻) (L = RC(NR')₂) have been widely investigated in main group metal, transition metal, and lanthanide metal chemistry due to their flexible steric and electronic properties, which can be easily tuned by variation of the organic substituents (R, R').¹ Moreover, their flexibility to coordinate either as mondentate two-electron donor (η^1) as well as chelating (η^2) or as bridging monodentate (μ - η^1 - η^1) four-electron donor² render these complexes very promising for technical applications in catalysis,³ often as cyclopentadienyl replacements, and material sciences.⁴ Considering these important applications, it came to us as a surprise that zinc amidinate complexes were almost unknown, whereas the corresponding guanidinate complexes and β -diketiminate complexes have been studied in more detail. They were shown to be of general interest for ROP catalysis of lactide⁵ and ε -caprolactone⁶ as well as in copolymerization reactions of CO_2 with epoxides, respectively.⁷

Recently, we started to investigate the synthesis of zinc amidinate complexes in more detail and reported on reactions of $ZnMe_2$ with different carbodiimides $C(NR)_2$ (R = *i*-Pr, ⁸Cy⁹), which unexpectedly proceeded with formation of novel cluster-type complexes such as $\{C[C(NR)_2ZnMe]\}_4$ (Figure 1). These are suitable starting reagents for the synthesis of the corresponding halide-substituted complexes $\{C[C(Ni-Pr)_2ZnX]\}_4$ (X = Cl, Br, I), which were obtained by Me/halide exchange reaction with AlX₃.¹⁰ In addition, heteroand homoleptic zinc complexes of the type [t-BuC(NR)2]ZnX and $[t-BuC(NR)_2]_2Zn$ (R = *i*-Pr, Cy; X = Cl, Br, I) were synthesized by salt elimination reaction, which represents the most common synthetic pathway for such complexes. Unfortunately, the synthesis of heteroleptic complexes LZnX is often complicated due to the formation of the corresponding homoleptic complexes L₂Zn.^{11,12}

Herein, we report on a straightforward synthetic route to heteroleptic zinc amidinate complexes of the type $[RC(NR')_2]$ -ZnX (X = I, Me), which were expected to be valuable starting reagents for further reactivity studies. In particular, complexes containing sterically demanding substituents were expected to

^{*}To whom correspondence should be addressed. Phone: +49 0201-1834635. Fax: +49 0201-1833830. E-mail: stephan.schulz@uni-due.de.

⁽¹⁾ See the following and references cited therein: (a) Edelmann, F. T. *Chem. Soc. Rev.* **2009**, *38*, 2253–2268. (b) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, *57*, 133–352. (c) Edelmann, F. T.; Coles, M. P. J. *Chem. Soc., Dalton Trans.* **2006**, 985–1001. (d) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219–300.

⁽²⁾ Further bindings modes see: Cole, M. L. J. Chem. Soc., Chem. Commun. 2007, 1579–1590.

^{(3) (}a) Coles, M. P.; Swenson, D. C.; Jordan, R. F. Organometallics **1997**, *16*, 5183–5194. (b) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. J. Am. Chem. Soc. **1998**, *120*, 9384–9385. (c) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. J. Am. Chem. Soc. **2000**, *122*, 274–289. (d) Foley, S. R.; Zhou, Y.; Yap, G. P. A.; Richeson, D. S. Inorg. Chem. **2000**, *39*, 924–929.

^{(4) (}a) Baunemann, A.; Bekermann, D.; Thiede, T. B.; Parala, H.; Winter, M.; Gemel, C.; Fischer, R. A. *J. Chem. Soc., Dalton Trans.* **2008**, 3715–3722. (b) Barker, J.; Blacker, N. C.; Phillips, N. C.; Alcock, N. W.; Errington, W.; Wallbridge, M. G. H. *J. Chem. Soc., Dalton Trans.* **1996**, 431–437.

^{(5) (}a) Coles, M. P.; Hitchcock, P. B. *Eur. J. Inorg. Chem.* 2004, *13*, 2662–2672.
(b) Aubrecht, K. B.; Chang, K.; Hillmyer, M. A.; Tolman, W. B. J. *J. Polym. Sci.* 2001, *39*, 284–293.
(c) Birch, S. J.; Boss, S. R.; Cole, S. C.; Coles, M. P.; Haigh, R.; Hitchcock, P. B.; Wheatley, A. E. H. *J. Chem. Soc., Dalton Trans.* 2004, *3*, 3568–3574.

⁽⁶⁾ Sanchez-Barba, L. F.; Alono-Moreno, C.; Garcés, A.; Fajardo, M.; Fernández-Baeza, J.; Otero, A.; Lara-Sánchez, A.; Rodríguez, A. M.; Lópex-Solera, I. J. Chem. Soc., Dalton Trans. 2009, 8054–8062.

⁽⁷⁾ See the following and references cited therein: (a) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. J. Organomet. Chem. **2003**, 683, 137–148. (b) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. Inorg. Chem. **2005**, 44, 8004–8010. (c) Liu, B. Y.; Tian, C. Y.; Zhanq, L.; Yan, W. D.; Zhanq, W. J. J. Polym. Sci., Part A: Polym. Chem. **2006**, 44, 6243–6251. (d) Kröger, M.; Folli, C.; Walter, O.; Döring, M. Adv. Synth. Catal. **2006**, 348, 1908–1918.

^{(8) (}a) Schulz, S.; Münch, M.; Flörke, U. Z. Anorg. Allg. Chem. 2008, 634, 2221–2225. (b) Münch, M.; Flörke, U.; Bolte, M.; Schulz, S.; Gudat, D. Angew. Chem. 2008, 120, 1535–1537. Angew. Chem., Int. Ed. 2008, 47, 1512–1516.

⁽⁹⁾ Schmidt, S.; Gondzik, S.; Schulz, S.; Bläser, D.; Boese, R. Organometallics 2009, 28, 4371–4376.

⁽¹⁰⁾ Gutschank, B.; Schulz, S.; Westphal, U.; Bläser, D.; Boese, R. Organometallics 2010, 29, 2093–2097.

⁽¹¹⁾ Eisenmann, T.; Khanderi, J.; Schulz, S.; Flörke, U. Z. Anorg. Allg. Chem. 2008, 634, 507–513.

⁽¹²⁾ Schmidt, S.; Schulz, S.; Bolte, M. Z. Anorg. Allg. Chem. 2009, 635, 2210–2213.



Figure 1. Typical structural motifs of zinc amidinate complexes. Amidinate units containing a delocalized π -electron system are accentuated.



Scheme 1. Synthesis of [{MeC(Ni-Pr)₂}ZnMe]₂, 1, and [MeC(Ni-Pr)₂]ZnI, 2^a

^{*a*} Amidinate units containing a delocalized π -electron system are accentuated.

be promising starting reagents for the synthesis of Zn-Zn bonded complexes by reductive coupling reaction as well as for halide and alkyl abstraction reactions.

Results and Discussion

Equimolar amounts of $[Me(C(Ni-Pr)_2]_2Zn \text{ and } ZnMe_2$ react at ambient temperature under ligand exchange and quantitative formation of the heteroleptic complex $[{MeC(Ni-Pr)_2}-ZnMe]_2, 1.1$ was then converted by reaction with an equimolar amount of I₂ into $[MeC(Ni-Pr)_2]ZnI, 2$. The ate-complex $[{MeC(Ni-Pr)_2}ZnI]_2LiI(OEt_2)_2, 3$, was obtained as a byproduct in low yield from an impure charge of $[MeC(Ni-Pr)_2]_2Zn$ containing LiI, which was formed by the reaction of Li[MeC-(NDipp)_2] with ZnI₂.^{11,12}

¹H and ¹³C NMR spectra of **1** showed resonances due to the amidinate ligand and the methyl group in the expected 1:1 ratio, whereas **2** showed only the resonances due to the amidinate ligand.

Single crystals of 1 and 3 were obtained from solutions in toluene (1) and toluene/Et₂O (3), respectively, upon storage at -30 °C. 1 crystallizes in the tetragonal space group $P4_32_12$ and 3 in the orthorhombic space group $P2_12_12_1$. 1 forms a centrosymmetric dimer in the solid state with bridging nitrogen atoms and a center of symmetry in the Zn₂N₂ ring, as was previously observed for [{*t*-BuC(N*i*-Pr)₂}ZnMe]₂.¹² The zinc atom in 3 is coordinated by one additional iodine and [Li(OEt₂)₂]⁺ as counterion, as was previously observed

in [*t*-BuC(NCy)₂ZnBrLiBr(OEt₂)₂]¹¹ and [Li(OEt₂)₂(μ -Cl)₂-Zn{N(Dipp)C(Me)]₂CH].¹³ The C–N bond lengths in **1** (C1–N1 1.301(2), C1–N2 1.367(2) Å) vary by almost 0.07 Å due to the differently coordinated N atoms, demonstrating the π -electrons within the NCN unit of the amidinate ligand to be rather localized than delocalized. The amidinate unit does not adopt a planar geometry, as is shown by the sum of the bond angles, which differ significantly. The three-coordinated carbon and nitrogen atoms in **3** (C1 359.9°; N1 359.0°) are almost planar, indicating sp²-hybridized centers, whereas the tetracoordinated nitrogen atom (N2 334.5°) shows a significantly smaller sum of bond angles.

The synthesis of heteroleptic zinc amidinate complexes LZnX via salt elimination reaction is often accompanied by the formation of the corresponding homoleptic zinc amidinate complex L_2Zn , which is sometimes difficult to separate. Therefore we became interested in a more straightforward route to amidinate zinc halide complexes. Hydrolysis of Li[*t*-BuC(NDipp)₂] yielded the free amidine **4**, which further reacts with ZnMe₂ with elimination of methane and subsequent formation of [*t*-BuC(NDipp)₂]ZnMe, **5**. **5** was isolated in good yield as a pale yellow crystalline solid. Reaction of **5** with an equimolar amount of I₂ yielded the iodine-bridged dimeric heteroleptic complex [{*t*-BuC(NDipp)₂Zn(μ -I)]₂, **7**, whereas addition

⁽¹³⁾ Prust, J.; Hohmeister, H.; Stasch, A.; Roesky, H. W.; Magull, J.; Alexopoulos, E.; Usón, I.; Schmidt, H.-G.; Noltemeyer, M. *Eur. J. Inorg. Chem.* **2002**, *8*, 2157–2162.



Figure 2. Solid-state structure of 1 (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity). Selected bond length (Å) and angles (deg): C1-N11.301(2), C1-N21.367(2), Zn1-N12.035(14), Zn1-N22.043(14), Zn1-C91.969(19), N1-C1-N2115.04(19), N1-Zn1-N260.22(5).



Figure 3. Solid-state structure of **3** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity). Selected bond length (Å) and angles (deg): C1–N1 1.283(4), C1–N2 1.406(4), C9–N3 1.323(4), Zn1–N1 2.073(3), Zn1–N2 2.125(7), Zn1–I1 2.545(5), Zn2–I2 2.671(4), Zn2–I3 (2.709(4), N1–C1–N2 112.40(3), N3–C9–N4 119.40(3), N1–Zn1–N2 64.34(11), I2–Zn2–I3 99.53(14).

of the Lewis base *tert*-butylpyridine yielded the expected monomeric, base-stabilized complex [*t*-BuC(NDipp)₂]Zn-Me(*t*-BuPy), **6**.

¹H and ¹³C NMR spectra of **5** and **6** show the resonances due to the amidinate ligand and the methyl group (and the pyridine base **6**) in the expected 1:1 intensities, whereas **7** shows only the resonances of the amidinate ligand. Single crystals were grown from solutions in toluene (**5**, **6**) and toluene/Et₂O (7) upon storage at -30 °C. **5** and **6** crystallize in the monoclinic space group $P2_1/c$; **7** crystallizes in the triclinic space group $P\overline{1}$.

In contrast to previously reported amidinate complexes,¹⁴ which typically showed N,N'-chelating amidinate moieties, the amidinate ligand in 5 coordinates in a rather unexpected η^1 -N, η^3 -arene fashion, clearly showing the expressed flexibility of amidinate ligands to adopt different coordination modes. As a consequence, 5 forms a five-membered ring with a localized C-N single bond (C1-N1 1.3736(16) Å) and a C=N double bond (C1-N2 1.2961(17) Å) within the amidinate moiety. In contrast, the heteroleptic amidinate complexes [MeC(Ni-Pr)2]ZnMe (1) and [t-BuC(Ni-Pr)2]ZnMe, which contain sterically less demanding amidinate ligands, show the expected N, N'-chelating modes.¹² Obviously, the η^1 -N, η^3 -arene binding mode reduces the ring strain compared to the N,N'-chelating mode (four-membered ring). A comparable structural motif was initially observed for the formamidinate complex [K{ η^{6} -Mes)-NC(H)N(Mes) { η^6 -Mes)NC(H)NH(Mes)], in which the potassium-cation coordinates to a single nitrogen atom and an additional π -coordinated aryl group.¹⁵ Recently this binding mode was also observed for indium and thallium amidinate complexes.¹⁶ While these findings are reasonable for large and soft (HSAB principle) metal centers, which rather tend to increase their coordination numbers, it is rather unexpected for Zn(II) centers. We therefore performed theoretical calculations on the η^1 -N, η^3 -arene (5') and the N,N' (5'') bonding isomers of 5. Both isomers are local minima of the potential energy surface; however, the N,N'-coordination mode (5'') was found to be energetically slightly preferred by 1.5 kcal. The central structural parameters calculated for the η^1 -N, η^3 -arene isomer (5'), which are summarized in Table 1, agree very well with the experimental data (full details are given in the Supporting Information).

The amidinate ligand in 7 exhibits a N,N'-chelating bonding mode, as was observed for $[{t-BuC(NDipp)_2}Zn(\mu-X)]_2(X =$ Cl,¹⁷ Br¹⁸). 7, which is isomorphous to the corresponding Cl- and Br-substituted complexes, forms an iodine-bridged dimer in the solid state with a center of inversion within the central Zn₂I₂ ring. In contrast, $[{t-BuC(Ni-Pr)_2}Zn(\mu-I)]_2^{12}$ as well as 3 form N-bridged dimers, clearly reflecting the role of the N-substituents. Sterically demanding Dipp groups prevent the formation of a sterically more hindered N-bridged dimer, which is typically formed in amidinates with sterically less demanding *i*-Pr substituents. The Zn–I bond lengths only slightly differ (Zn1-I1 2.6078, Zn1-I2 2.6153 Å), and the C-N bond lengths within the amidinate moiety (C1-N1 1.348(3), C1-N2 1.328(3) Å) are in between typical values for a C–N single bond and a C=N double bond, indicating an almost perfect delocalization of the π -electrons within the CN₂ backbones of the four-membered rings. Analogous findings were reported for $[{t-BuC(NDipp)_2}Zn(\mu-X)]_2 (X = Cl, {}^{17}Br^{18})$. In the base-stabilized complex 6, the Zn atom is electronically saturated by coordination of the Lewis base tert-butylpyridine. As a consequence, the coordination mode of the amidinate unit rearranges from a η^1 -N, η^3 -arene fashion to a N,N'-chelating

Dale, S. H. Inorg. Chem. 2007, 46, 9988–9997.

 ⁽¹⁴⁾ Lesikar, L. A.; Richards, A. F. *Polyhedron* 2010, *29*, 1411–1422.
 (15) Baldemus, J.; Berghof, C.; Cole, M. L.; Evans, D. J.; Hev-Hawkins,

⁽¹⁵⁾ Baldemus, J.; Berghol, C.; Cole, M. L.; Evans, D. J.; Hey-Hawkins E.; Junk, P. C. J. Chem. Soc., Dalton Trans. 2002, 2802–2804.

⁽¹⁶⁾ Jones, C.; Junk, P. C.; Platts, J. A.; Rathmann, D.; Stasch, A. J. Chem. Soc., Dalton Trans. 2005, 2497–2499.

⁽¹⁷⁾ Nimitsiriwat, N.; Gibson, V. C.; Marshall, E. L.; Takolpckdee, P.; Tomov, A. T.; White, A. J. P.; Williams, D. J.; Elsegood, M. R. J.;

⁽¹⁸⁾ Jones, C.; Furness, L.; Nembenna, S.; Rose, R. P.; Aldridge, S.; Stasch, A. J. Chem. Soc., Dalton Trans. 2010, 39, 8788-8795.

Scheme 2. Synthesis of 5, 6, 7, and 8^{a}



^{*a*} Conditions: (i) ZnMe₂, toluene, (ii) I₂, toluene, (iii) *tert*-butylpyridine, toluene, (iv) $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, CH₂Cl₂. Amidinate units containing a delocalized π -electron system are accentuated.





Figure 5. Solid-state structure of **6** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity). Selected bond length (Å) and angles (deg): C1–N1 1.358(3), C1–N2 1.328(3), N1–C2 1.424(3), N2–C14 1.426(3), Zn1–N1 2.003(2), Zn1–N2 2.0022(19), Zn1–I1 2.6153(3), N1–C1–N2 (109.8(2), C1–N1–C14 39.840(36), C1–N2–C2 133.0(2), N1–Zn1–N2 66.27(8).

Figure 4. Solid-state structure of **5** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity). Selected bond length (Å) and angles (deg): C1–N1 1.3736(16), C1–N2 1.2961(17), N1–C14 1.4387(16), N2–C2 1.4011(17), Zn1–N1 1.9077(11), Zn1–C2 2.4311(12), Zn1–C3 2.7652(14), Zn1–C7 2.7223(13), Zn1–C26 1.9302(14), N1–C1–N2 121.16(12), C1–N1–C2 120.31(11), C1–N1–C14 125.43(11).

mode (C1–N1 1.3423(16), C1–N2 1.3393(16) Å) with almost perfectly delocalized π -electrons.

Cationic amidinate metal complexes have been investigated in the past due to their capacity to serve as activators for catalytic reactions.¹⁹ We therefore investigated the reaction of **5** with one equivalent of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, which was recently shown to effectively protonate $\text{Cp}_2^2\text{Zn}_2^{,20}$ Even though the formation of methane was observed, the reaction proceeded with protonation of the amidinate ligand and subsequent formation of the amidinium salt [*t*-BuC-{N(H)Dipp}₂][Al{OC(CF₃)₃}₄], **8**, rather than with formation of the expected cationic zinc complex [{*t*-BuC(NDipp)₂}Zn]-[Al{OC(CF₃)₃}₄]. A comparable finding has been previously reported for the reaction of the zinc guanidinate with 2,6-di-*tert*butylphenol (HOR),^{5a} even though this reaction occurred with protonation of only one nitrogen atom and subsequent formation of the guanidine Me₂NC(N*i*-Pr)(NH*i*-Pr), which

^{(19) (}a) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. J. Am. Chem. Soc. **1998**, *120*, 9384–9385. (b) Baugh, L. S.; Sussano, J. A. J. Polym. Sci. **2002**, *40*, 1663.

⁽²⁰⁾ Schulz, S.; Schuchmann, D.; Krossing, I.; Himmel, D.; Bläser, D.; Boese, R. Angew. Chem. **2009**, *121*, 5859–5862. Angew. Chem., Int. Ed. **2009**, *48*, 5748–5741.



Figure 6. Solid-state structure of **7** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity). Selected bond length (Å) and angles (deg): C1–N1 1.3423(16), C1–N2 1.3393(16), N1–C2 1.4223(16), N2–C14 (1.4194(16), Zn1–N1 2.0922(11), Zn1–N2 2.067(11), Zn1–C39 1.9710(15), Zn1–N3 2.1316(12), N1–C1–N2 110.63(11), C1–N1–C2 128.63(11), C1–N2–C14 130.47(10), N1–Zn1–N2 64.03(4).



Figure 7. Solid-state structure of 8 (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity except for H1 and H2). H1 and H2 were located in the electron difference map. Selected bond length (Å) and angles (deg): C1-N1 1.326(4), C1-N2 1.331(4), N1-H1 0.873(10), N2-H2 0.885(10), N1-C11 1.452(5), N2-C21 1.454(4), N1-C1-N2 116.8(3), C1-N2-C21 129.2(3), C1-N1-C11 125.8(3), C1-N2-H2 112(3).

coordinates to the zinc alkoxide with formation of $[MeZn(OAr) \cdot {Me_2NC(Ni-Pr)(NHi-Pr)}]$. The formation of **8** containing an amidinium cation clearly shows the improved protonation capability of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$ compared to the simple alcohol HOR. The formation of **8** requires three equivalents of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, and indeed, when **4** was reacted with three equivalents of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, and indeed, when **4** was reacted with three equivalents of $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$, **8** was formed in almost quantitative yield. The ¹H NMR spectrum of **8** showed two new resonances at 7.72 and 7.37 ppm for the N–H groups. Obviously, both the methyl group and the Lewis-basic N

Table 1. Selected Experimental and Calculated Structural Parameters of 5 and 5'

	5	5′
	Bond length [Å]	
Zn-C10	1.9302(14)	1.9615
Zn-N2	1.9077(11)	1.9528
C1-N2	1.3736(16)	1.3749
N2-C3	1.4387(16)	1.4337
C1-N1	1.2961(17)	1.3025
N1-C4	1.4011(17)	1.3889
Zn-C4	2.4311(12)	2.4787
Zn-C5	2.7223(13)	2.779
Zn1-C6	3.3046(14)	3.354
Zn-C7	3.5811(14)	3.649
Zn-C8	3.3274(16)	3.424
Zn-C9	2.7652(14)	2.866
	Bond Angles (deg)	
N1-C1-N2	121.16(12)	120.8894
Zn-N2-C1	120.01(9)	118.7591
C1-N1-C4	120.31(11)	123.7574
C10-Zn-N2	154.48(6)	153.981

Scheme 3



atoms of the amidinate ligand were protonated under these reaction conditions. Monitoring the reaction by temperaturedependent NMR spectroscopy starting at -70 °C could not clarify whether the methyl group or the N atoms are protonated first. The IR spectrum of **8** showed characteristic absorption bands of a N–H bond at 3327 and 3290 cm⁻¹.

Single crystals of **8** were obtained from a solution in CH_2Cl_2 at -30 °C. Complex **8** crystallizes in the monoclinic space group $P2_1$. The π -electrons within the NCN backbone are almost perfectly delocalized (C1–N1 1.326(4), C1–N2 1.331(4) Å). The N–C–N bond angle of 116.8(3)° and the N–C_{ipso} bond distances of 1.452(5) and 1.454(4) Å are similar to those reported for the neutral amidine (N–C–N 119.1(2)°, N–C_{ipso} 1.433(3) Å).²¹

The heteroleptic amidinate zinc halides were expected to be valuable starting reagents for the synthesis of compounds containing a central Zn–Zn bond, as was initially reported by Carmona et al. for dizincocene $[Cp*_2Zn_2]$.²² Since then, several complexes containing Zn atoms in the formal oxidation state +1 have been prepared, most of them by reductive (Wurtzanalogous) coupling reaction²³ and substitution reaction using $Cp*_2Zn_2$.²⁴ Unfortunately, several attempts to reduce the heteroleptic complexes LZnI remained unsuccessful. Reactions of 7 with Na, K, KC₈, and Na-naphthalene at different reaction

⁽²¹⁾ Xia, A.; El-Kaderi, H. M.; Heeg, M. J.; Winter, C. H. J. Organomet. Chem. 2003, 682, 224–232.

⁽²²⁾ Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. Science **2004**, *305*, 1136–1138.

temperatures (25, 60, 110 °C) and times (2, 4, 12 h) in different solvents (toluene, THF, hexane) yielded only elemental zinc and so far unidentified products. Comparable findings have very recently been reported by Jones et al. for reduction reactions of $[{t-BuC(NDipp)_2}Zn(\mu-Br)]_2$.¹⁸

Conclusion

Heteroleptic zinc amidinate complexes LZnMe (1, 5) were synthesized in good yields either by ligand exchange reaction between L₂Zn (L = amidinate) and ZnMe₂ or by methane elimination reaction of ZnMe₂ with LH and structurally characterized. Unexpectedly, the amidinate ligand in 5 coordinates in a η^1 -N, η^3 -arene mode, as was shown by single-crystal X-ray diffraction. The corresponding iodine-substituted zinc amidinate complexes (2, 3, 7) were accessible from reaction between 1 and 5, respectively, with iodine. 5 was also found to react with the Lewis base *tert*-butylpyridine with formation of the Lewis acid—base adduct 6, in which the amidinate group adopts an N, N'-chelating binding mode. Reaction of 5 with [H(OEt₂)₂][Al-{OC(CF₃)₃}₄] occurred with protonation of both N atoms and subsequent formation of complex 8.

Experimental Details

All manipulations were performed in a glovebox (MBraun) under Ar atmosphere or using standard Schlenk line techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. A 1.2 M solution of ZnMe₂ in toluene and I2 were obtained from Acros and used as received, whereas tert-butylpyridine (Arcos) was distilled and carefully dried over activated molecular sieves prior to use. Li amidinates $Li[RC(NR')_2]$ (R = Me, t-Bu; R' = i-Pr, Dipp) were generally prepared by reaction of the carbodiimide with the corresponding organolithium compound,^{3a} and [MeC(Ni-Pr)₂]₂Zn was prepared by reaction of two equivalents of Li[MeC(Ni-Pr)2] with pared by feaction if two equivalents of EquiveC((3741_{21}) with ZnI_2 .^{8a} [H(OEt_2)₂][Al{ $OC(CF_3)_3$ }] was prepared according to a procedure described by Krossing et al.²⁵ A Bruker DMX 300 was used for NMR spectroscopy. ¹H and ¹³C{¹H} NMR spectra were referenced to internal C₆D₅H (¹H: $\delta = 7.154$; ¹³C: $\delta = 128.0$), CD_2Cl_2 (¹H: $\delta = 5.32$; ¹³C: $\delta = 53.5$), and THF- d_8 (¹H: $\delta = 3.580$, 1270; ¹³C: $\delta = 25.2$, ⁶⁷A). ¹³C: $\delta = 3.580$, 1.730; ^{f3}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 per-

(24) (a) Schulz, S.; Schuchmann, D.; Westphal, U.; Bolte, M. Organometallics 2009, 28, 1590–1592. (b) Carrasco, M.; Peloso, R.; Rodríguez, A.; Álvarez, E.; Maya, C.; Carmona, E. Chem.—Eur. J. 2010, 16, 9754–9757. (c) Schulz, S.; Gondzik, S.; Schuchmann, D.; Westphal, U.; Dobrzycki, L.; Boese, R.; Harder, S. Chem. Commun. 2010, 46, 7757–7759. (25) Krossing, I.; Reininger, A. Eur. J. Inorg. Chem. 2005, 120, 1979–1989.

formed at the "Elementaranalyse Labor" of the University of Essen.

[{ $MeC(Ni-Pr)_2$ } $ZnMe]_2$, **1**. $ZnMe_2$ (4.2 mL, 1.2 M in toluene, 5 mmol) was added to a solution of [$Me(C(Ni-Pr)_2)_2Zn$ (1.86 g, 5 mmol) in 20 mL of toluene at ambient temperature and stirred for an additional 2 h. The solution was concentrated under vacuum and stored at -30 °C. Colorless crystals of 1 were formed within 24 h.

Yield: 2.01 g (91%). Melting point: 76 °C. Anal. Found (calcd) for $C_{18}H_{40}N_4Zn_2$ (443.28 g/mol): H, 9.2 (9.1); C, 49.0 (49.0); N, 12.5 (12.5). ¹H NMR (300 MHz, C_6D_6 , 25 °C): δ –0.14 (s, 3H, Zn*CH*₃), 1.10 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂), 1.53 (s, 3H, CH₃), 3.23 (sept, ³J_{HH} = 6.3 Hz, 2H, CH(CH₃)₂). ¹³C NMR (125 MHz, C_6D_6 , 25 °C): δ –8.6 (ZnCH₃), 14.3 (CH(CH₃)₂), 25.5 (CH₃), 48.4 (CH(CH₃)₂), 171.0 (NCN). IR: ν 2961, 2930, 2896, 2867, 1555, 1509, 1452, 1377, 1361, 1342, 1314, 1287, 1259, 1172, 1135, 1122, 1011, 808, 640, 575, 520, 485, 448 cm⁻¹.

[MeC(N*i*-Pr)₂]ZnI, 2. A solution of I₂ (1.27 g, 5 mmol) in 20 mL of Et₂O was added dropwise to 1 (2.21 g, 5 mmol) dissolved in 20 mL of Et₂O at -30 °C. The resulting mixture was warmed to ambient temperature and stirred for an additional 12 h. The solution was concentrated under vacuum and stored at -30 °C. 2 was isolated as a colorless, crystalline solid.

Yield: 1.58 g (95%). Melting point: > 220 °C. Anal. Found (calcd) for C₈H₁₇N₂IZn (333.51 g/mol): H, 5.2 (5.1); C, 28.8 (28.8); N, 8.3 (8.4). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.14 (d, ³J_{HH} = 6.3 Hz, 12H, CH(CH₃)₂), 1.40 (s, 3H, CH₃), 3.23 (sept, ³J_{HH} = 6.4 Hz, 2H, CH(CH₃)₂). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ 15.3 (CH(CH₃)₂), 25.0 (CCH₃), 48.4 (CH(CH₃)₂), 176.0 (NCN). IR: ν 3058, 3029, 2963, 2123, 2103, 1649, 1622, 1584, 1544, 1484, 1439, 1320, 1296, 1201, 1168, 1155, 1097, 1070, 1025, 898, 826, 750, 687, 620, 598, 529, 513, 490 cm⁻¹.

[{ $MeC(Ni-Pr)_2$ }ZnI]₂LiI(OEt)₂, 3. 3 was obtained as a byproduct in the synthesis of [MeC(N*i*-Pr)₂]ZnI, 2. Colorless crystals of 3 were formed within 24 h in less than 5% yield. In addition, 3 was synthesized by reaction of 2 with an equimolar amount of LiI in refluxing Et₂O for 24 h. The reaction solution was filtered, and all volatiles were removed under vacuum, yielding a colorless solid. Unfortunately, this reaction product also contained 2 and the homoleptic complex [MeC(N*i*-Pr)₂]₂Zn to some extent (15–20%), as was shown by ¹H NMR spectroscopy. This finding also explains the unsatisfactory elemental analysis that was obtained for 3.

Melting point: 80 °C (dec). Anal. Found (calcd) for $C_{24}H_{54}N_4I_3$. LiO₂Zn₂ (949.09 g/mol): H, 5.3 (5.7); C, 29.1 (30.4); N, 5.3 (5.9). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.05 (d, ³J_{HH} = 6.0 Hz, 12H, CH(CH₃)₂), 1.11 (t, 6H, OCH₂CH₃), 1.26 (d, ³J_{HH} = 6.7, 12H, CH(CH₃)₂), 1.82 (s, 3H, CH₃), 2.02 (s, 3H, CH₃), 3.38 (q, 4H, OCH₂CH₃), 3.38 (sept, 2H, CH(CH₃)₂), 3.76 (sept, ³J_{HH} = 6.5 Hz, 2H, CH(CH₃)₂). ¹³C NMR data could not be obtained due to the very low solubility of **3**. IR: ν 2962, 2926, 2890, 2869, 1605, 1496, 1455, 1378, 1362, 1319, 1260, 1174, 1121, 1089, 1060, 1010, 877, 793, 642, 602, 577, 516, 475 cm⁻¹.

t-BuC(NHDipp)(NDipp), 4. A solution of Li[*t*-BuC(NDipp)₂] (2.13 g, 5 mmol) in 30 mL of Et₂O was added to a mixture of 80 mL of Et₂O and 20 mL of H₂O and vigorously stirred for 30 min. The organic phase was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried with MgSO₄ and filtered, and all volatiles were evaporated under vacuum, yielding 4 as a colorless, crystalline solid.

Yield: 1.83 g (87%). Melting point: 138 °C. Anal. Found (calcd) for C₂₉H₄₄N₂ (420.68 g/mol): H, 10.3 (10.5); C, 83.0 (82.8); N, 6.7 (6.7). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.35 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.44 (s, 9H, C(CH₃)₃), 3.40 (sept, 2H, CH(CH₃)₂), 3.58 (sept, ³J_{HH} = 6.4 Hz, 2H, CH(CH₃)₂), 5.55 (s, 1H, NH), 7.00–7.44 (m, 6H, ArH). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ 21.7 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 29.0 (CH(CH₃)₃), 30.1 (C(CH₃)₃), 39.6 (C(CH₃)₃), 136.4 (Ar-C), 138.5 (Ar-C), 144.8 (Ar-C), 147.9 (Ar-C), 159.1 (NCN). IR: v 3337

^{(23) (}a) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; del Río, D.; Andersen, R. A. J. Am. Chem. Soc. 2007, 129, 693–703. (b) Wang, Y.; Quillian, B.; Wei, P.; Wang, H.; Yang, X.-J.; Xie, Y.; King, R. B.; Schleyer, P. v. R.; Schaefer, H. F., III; Robinson, G. H. J. Am. Chem. Soc. 2005, 127, 11944–11945. (c) Zhu, Z.; Wright, R. J.; Olmstead, M. M.; Rivard, E.; Brynda, M.; Power, P. P. Angew. Chem., Int. Ed. 2006, 45, 5807–5810. (d) Zhu, Z.; Brynda, M.; Wright, R. J.; Fischer, R. C.; Merrill, W. A.; Rivard, E.; Wolf, R.; Fettinger, J. C.; Olmstead, M. M.; Power, P. P. J. Am. Chem. Soc. 2007, 129, 10847–10857. (e) Yang, X.-J.; Yu, J.; Liu, Y.; Xie, Y.; Schaefer, H. F., III; Liang, Y.; Wu, B. J. Chem. Soc., Chem. Commun. 2007, 2363–2365. (f) Tsai, Y.-C.; Lu, D.-Y.; Lin, Y.-M.; Hwang, J.-K.; Yu, J.-S. K. J. Chem. Soc., Chem. Commun. 2007, 4125–4127. (g) Fedushkin, I. L.; Skatova, A. A.; Ketkov, S. Y.; Eremenko, O. V.; Piskunov, A. V.; Fukin, G. K. Angew. Chem., Int. Ed. 2007, 46, 4302–4305. (h) Yu, J.; Yang, X.-J.; Liu, Y.; Pu, Z.; Li, Q.-S.; Xie, Y.; Schaefer, H. F.; Wu, B. *J. Chem. Soc.*, Dalton Trans. 2009, 5773–5779. (j) Liu, Y.; Li, S.; Yang, X.-J.; Yang, P.; Gao, J.; Xia, Y.; Wu, B. Organometallics 2008, 28, 5270–5272.

(N-H), 3064, 2959, 2867, 2166, 1656, 1610, 1584, 1457, 1432, 1321, 1255, 1211, 1097, 799, 755, 724 cm⁻¹.

 $[t-BuC(NDipp)_2]ZnMe, 5. ZnMe_2 (4.2 mL, 1.2 M in toluene, 5 mmol) was added to a solution of 4 (2.10 g, 5 mmol) in 20 mL of toluene at ambient temperature and stirred for 2 h. The solution was concentrated under vacuum and stored at <math>-30$ °C. Colorless crystals of 5 were formed within 24 h.

Yield: 2.38 g (95%). Melting point: 143 °C. Anal. Found (calcd) for $C_{30}H_{46}N_2Zn$ (500.06 g/mol): H, 9.3 (9.3); C, 72.5 (72.1); N, 5.6 (5.6). ¹H NMR (300 MHz, C_6D_6 , 25 °C): δ –1.06 (s, 3H, Zn*CH*₃), 1.04 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.27 (d, ³J_{HH} = 6.9 Hz, 6H, CH(CH₃)₂), 1.28 (d, ³J_{HH} = 7.1 Hz, 6H, CH(CH₃)₂), 1.33 (d, ³J_{HH} = 6.8 Hz, 6H, CH(CH₃)₂), 1.38 (s, 9H, C(CH₃)₃), 3.24 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 3.58 (sept, ³J_{HH} = 6.9 Hz, 2H, CH(CH₃)₂), 2.59 °C): δ 1.4 (ZnCH₃), 21.8 (CH(CH₃)₂), 22.2 (CH(CH₃)₂), 24.1 (CH(CH₃)₂), 26.3 (CH(CH₃)₂), 28.3 (CH(CH₃)₂), 28.9 (CH-(CH₃)₂), 31.4 (C(CH₃)₃), 41.6 (C(CH₃)₃), 123.4 (Ar-*C*), 125.4 (Ar-*C*), 126.1 (Ar-*C*), 128.1 (Ar-*C*), 168.1 (NCN). IR: ν 3027, 2961, 1534, 1495, 1459, 1435, 1081, 1030, 726, 693, 463 cm⁻¹.

 $[t-BuC(NDipp)_2]ZnMe(t-BuPy), 6. tert-Butylpyridine (0.63 g, 5 mmol) was added dropwise to 5 (2.50 g, 5 mmol) dissolved in 20 mL of toluene. The resulting solution was stirred for 2 h, concentrated under vacuum, and stored at -30 °C. Colorless crystals of 6 were formed within 24 h.$

Yield: 2.86 g (90%). Melting point: > 220 °C. Anal. Found (calcd) for C₃₉H₅₉N₃Zn (635.26 g/mol): H, 9.2 (9.4); C, 73.2 (73.7); N, 6.5 (6.6). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ –1.06 (ZnCH₃), 0.98 (s, 9H, *t*-BuPy), 1.02 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.12 (s, 9H, C(CH₃)₃), 1.41 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 3.87 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 6.82 (dd, ³J_{HH} = 6.2 Hz, ³J_{HH} = 2.8 Hz, 2H, *t*-BuPy), 7.00 (t, 4H, Ar-H), 7.25 (d, ³J_{HH} = 6.8, 4H, Ar-H), 8.60 (dd, ³J_{HH} = 6.2 Hz, 2H, *t*-BuPy). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ 1.1 (ZnCH₃), 21.5 (CH(CH₃)₂), 22.0 (CH(CH₃)₂), 23.8 (CH(CH₃)₂), 26.0 (CH(CH₃)₂), 28.7 (CH(CH₃)₂), 30.0 (CH-(CH₃)₂), 31.1 (C(CH₃)₃), 41.6 (C(CH₃)₃), 120.4 (Ar-C), 123.1 (Ar-C), 139.0 (Ar-C) 149.9 (Ar-C), CN₂ not observed. IR: ν 2963, 2866, 1614, 1432, 1404, 1360, 1304, 1275, 1262, 1240, 1211, 1172, 1095, 1075, 1019, 973, 830, 802, 759, 727, 655, 632, 572, 521, 428 cm⁻¹.

{[*t*-BuC(NDipp)₂]Zn(μ -I)}₂, **7**. A solution of I₂ (1.27 g, 5 mmol) in 20 mL of toluene was added dropwise at -30 °C to **5** (2.50 g, 5 mmol) dissolved in 20 mL of toluene. The resulting mixture was warmed to ambient temperature and stirred for an additional 12 h. The suspension was filtered, and the resulting solid was recrystallized from a solution in toluene/Et₂O at -30 °C. Colorless crystals of **7** were formed within 24 h.

Yield: 5.45 g (89%). Melting point: > 220 °C. Anal. Found (calcd) for $C_{58}H_{86}N_4Zn_2$ (1223.85 g/mol): H, 7.2 (7.1); C, 57.0 (56.9); N, 4.5 (4.6). ¹H NMR (300 MHz, THF- d_8 , 25 °C): δ 0.95 (s, 9H, C(CH₃)₃), 1.20 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.33 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 3.62 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 7.01-7.19 (m, 6H, Ar-H). ¹³C NMR (125 MHz, C₆D₆, 25 °C): δ 23.0 (CH(CH₃)₂), 27.6 (CH(CH₃)₂), 29.1 (CH-(CH₃)₂), 30.9 (C(CH₃)₃), 41.6 (C(CH₃)₃), 123.9 (Ar-C), 125.0 (Ar-C), 129.0 (Ar-C), 129.7 (Ar-C), CN₂ not observed. IR: ν 2957, 2924, 2865, 1617, 1491, 1462, 1438, 1363, 1310, 1254, 1235, 1211, 1178, 1098, 1053, 1030, 975, 932, 800, 755, 706, 431, 410 cm⁻¹.

[*t*-BuC{N(H)Dipp}₂][Al{OC(CF₃)₃}₄], 8. A solution of [H(OEt₂)₂][Al{OC(CF₃)₃}₄] (3.28 g, 3 mmol) in 10 mL of CH₂Cl₂ was added dropwise at -50 °C to 5 (0.50 g, 1 mmol) dissolved in 10 mL of CH₂Cl₂ and stirred for 1 h at -50 °C. The resulting solution was warmed to ambient temperature, stirred for an additional 60 min, concentrated under vacuum, and stored at -30 °C. Colorless crystals of 8 were formed within 48 h.

Yield (isolated crystals): 0.83 g (60%). Melting point: > 220 °C. Anal. Found (calcd) for $C_{45}H_{45}AlF_{36}N_4O_4$ (1388.81 g/mol): H, 3.1 (3.2); C, 38.1 (38.1); N, 3.9 (4.0). ¹H NMR (300 MHz, CD₂Cl₂, 25 °C): δ 1.03 (d, ³*J*_{HH} = 6.7 Hz, 6H, CH(CH₃)₂), 1.27 (d, ³*J*_{HH} = 6.7 Hz, 6H, CH(CH₃)₂), 1.27 (d, ³*J*_{HH} = 6.7 Hz, 6H, CH(CH₃)₂), 1.44 (s, 9H, C(CH₃)₂), 1.47 (d, ³*J*_{HH} = 6.7 Hz, 6H, CH(CH₃)₂), 2.84 (sept, ³*J*_{HH} = 6.8 Hz, 2H, CH(CH₃)₂), 2.92 (sept, ³*J*_{HH} = 6.8 Hz, 2H, CH(CH₃)₂), 7.37 (s, 1H, NH), 7.24–7.62 (m, 6H, Ar-H), 7.64 (s, 1H, NH). ¹⁹F{¹H} (235 MHz, CD₂Cl₂, 25 °C): δ –74.6. IR: ν 3327, 3290, 2970, 1560, 1576, 1351, 1297, 1274, 1239, 1212, 1173, 970, 832, 803, 726, 559, 535, 444 cm⁻¹.

Single-Crystal X-ray Analyses. Crystallographic data for 1, 3, 5, 6, and 7 were collected on a Bruker AXS SMART APEX CCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å; T = 173(2) K). Data for 8 were collected with a STOE IPDS-II diffractometer. Crystallographic data for 1, 3, 5, 6, 7, and 8 are given in the Supporting Information. The structures were solved by direct methods (SHELXS-97)²⁶ and refined by full-matrix least-squares on F^2 . Semiempirical absorption corrections were applied. All nonhydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).²⁷

Computational Calculations

DFT calculations were carried out with the Gaussian03 suite of programs (M. J. Frisch, et al., Gaussian03, Revision D.02; Gaussian Inc., Pittsburgh, PA, 2003). The molecular structures of 5' and 5'' were obtained by performing a complete energy optimization of all geometric parameters at the b3lyp/svp level; SVP is the split-valence basis set with the additional polarization functions of Ahlrichs et al. Atomic charges of 5' and 5'', which were calculated from NBO population analyses, are given in the Supporting Information.

The crystallographic data of the structures (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-785891 (1), CCDC-785892 (3), CCDC-785893 (5), CCDC-785895 (6), CCDC-785894 (7), and CCDC-785458 (8). 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; e-mail for inquiry: fileserv@ccdc.cam.ac.uk; e-mail for deposition: deposit@ccdc.cam.ac.uk).

Acknowledgment. S. Schulz thanks the German Science Foundation (DFG) for financial support.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

⁽²⁶⁾ Sheldrick, G. M. Acta Crystallogr., Sect. A 1990, 46, 467.
(27) Sheldrick, G. M. SHELXL-97, Program for Crystal Structure Refinement; Universität Göttingen, 1997.