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Synthesis and X-ray crystal structures of heteroleptic zinc amidinate complexes

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Abstract

The synthesis of heteroleptic zinc amidinate complexes is reported. Reactions of LZnI [L=*t*-BuC(NDipp)$_2$; Dipp=2,6-*i*-Pr$_2$-C$_6$H$_3$] with diisopropylcarbodiimide (*i*-PrN)$_2$C yielded the Lewis acid-base adduct LZn(I)-N(*i*-Pr)CN(*i*-Pr) **1**. In addition, the synthesis of LZnN(SiMe$_3$)$_2$ **2** and its reaction with (*i*-PrN)$_2$C, which occurred with formation of the heteroleptic amidinate-guanidinate complex LZnL′ **3** [L′=(Me$_3$Si)$_2$NC(N*i*-Pr)$_2$], is reported. Compounds **1–3** were characterized by nuclear magnetic resonance (^{1}H, ^{13}C) and infrared spectroscopy, elemental analysis, and single crystal X-ray diffraction (**1** and **2**), respectively.

Keywords: amidinate; crystal structure; zinc.

Introduction

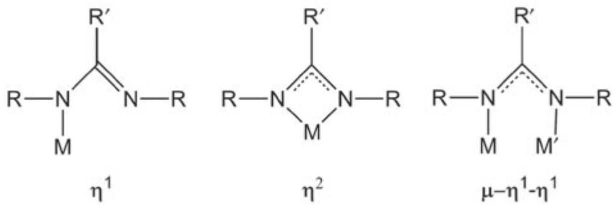
Monoanionic amidinates (L$^-$) [L$^-$=RC(NR′)$_2^-$] are well-established chelating organic ligands in main group metal and transition metal chemistry. Their steric and electronic properties can easily be modified by variation of the organic substituents (R, R′) (see review articles by Barker and Kilner, 1994; Coles, 2006; Edelmann, 2008, 2009) and they were found to bind either as monodentate two-electron donor (η^1), chelating (η^2), or bridging monodentate (μ-η^1-η^1) four-electron donor (Scheme 1). Further binding modes have been summarized by Junk and Cole (2007). According to their flexible properties, amidinate complexes are of potential interest for technical applications in catalysis (Coles et al., 1997; Radzewich et al., 1998; Dagorne et al., 2000; Foley et al., 2000) and material sciences (Barker et al., 1996; Baunemann et al., 2008). Surprisingly, zinc amidinate complexes were almost unknown until we and others started to investigate them in more detail. Reactions of ZnMe$_2$ with carbodiimides C(NR)$_2$ (R=Et, *i*-Pr, Cy, Ph) unexpectedly yielded multinuclear complexes such as {C[C(NR)$_2$ZnMe]}$_4$ (Münch et al., 2008; Schmidt et al., 2009b, 2011), which were shown by Gutschank et al. (2010a,b) to be suitable starting reagents for the synthesis of the corresponding halide-, hydride-, and acetylide-substituted derivatives {C[C(N*i*-Pr)$_2$ZnX]}$_4$ (X=Cl, Br, I; H, CCH, CCPh). Moreover, hetero- and homoleptic zinc complexes of the type LZnX and L$_2$Zn were synthesized by salt and alkane elimination reactions (Eisenmann et al., 2008; Schulz et al., 2008; Schmidt et al., 2009a,b, 2010; Jones et al., 2010).

Herein we report on reactions of LZnI [L=*t*-BuC(NDipp)$_2$; Dipp=2,6-*i*-Pr$_2$-C$_6$H$_3$] with (*i*-PrN)$_2$C, yielding the expected Lewis acid-base adduct LZn(I)-N(*i*-Pr)CN(*i*-Pr) **1**. In addition, the synthesis of the heteroleptic zinc amidinate complex LZnN(SiMe$_3$)$_2$ **2** and its reaction with (*i*-PrN)$_2$C, which occurred with formation of the heteroleptic bis(amidinate) complex LZnL′ **3** [L′=(Me$_3$Si)$_2$NC(N*i*-Pr)$_2$], is described.

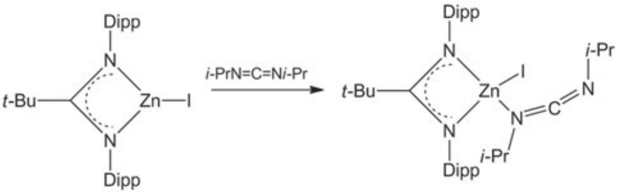
Results and discussion

Equimolar amounts of LZnI [L=*t*-BuC(NDipp)$_2$; Dipp=2,6-*i*-Pr$_2$-C$_6$H$_3$] and diisopropylcarbodiimide (*i*-PrN)$_2$C reacted at ambient temperature with formation of the expected Lewis acid-base adduct LZn(I)-N(*i*-Pr)CN*i*-Pr **1**, which was obtained as a colorless crystalline solid after storage at 4°C in almost quantitative yield (Scheme 2). The ^{1}H spectrum of **1** showed resonances due to the amidinate ligand (L) and the carbodiimide in the expected 1:1 ratio. The ^{13}C nuclear magnetic resonance (NMR) spectrum shows a characteristic resonance at 147.7 ppm due to the presence of a carbodiimide moiety, which is supported by the IR spectrum of **1**, showing a characteristic absorption band due to the N=C=N unit of the carbodiimide at 2139 cm^{-1}.

Carbodiimide adducts of metal complexes are of particular interest as experimental findings and theoretical calculations on reactions of carbodiimides with organoboron and -aluminum compounds proved the insertion reaction most likely to proceed via initial formation of a Lewis acid-base adduct (Hill et al., 2005; Rowley et al., 2005; Pierce et al., 2007). Moreover, Lechler et al. (1989) demonstrated that the Lewis acidity of the metal complex plays an important role on the reaction pathway, demonstrating that AlMe$_3$ reacts with (Me$_3$SiN)$_2$C with insertion in the Al-Me bond and subsequent formation of [MeC(NSiMe$_3$)$_2$]AlMe$_2$, whereas GaMe$_3$ and InMe$_3$ yielded the 1:1 adducts Me$_3$M-N(SiMe$_3$)=C=NSiMe$_3$, respectively. In contrast, AlMe$_3$ was found to react with *N*,*N*′-dialkylcarbodiimides (RN)$_2$C (R=*i*-Pr, Cy) with formation of the Lewis acid-base adducts (Kottmair-Maieron, 1987). Unfortunately, these adducts are often reaction intermediates. As a consequence, only six adducts were structurally characterized to date (Anderson and Einstein, 1978; Hausen et al., 1986; Hill et al., 2005; Schulz et al., 2008; Neumüller and Dehnicke, 2010; Pi et al., 2010). Therefore, we became interested in the solid-state structure of **1**.



Scheme 1 Typical binding modes in metal amidinate complexes.



Scheme 2 Synthesis of **1**.

Single crystals of **1** were obtained from a solution in toluene upon storage at 4°C (Figure 1). Compound **1**, which represents only the second example of a carbodiimide-zinc adduct, crystallizes in the orthorhombic space group $P2_12_12_1$. Compound **1** is monomeric in the solid state, whereas the starting reagent LZnI adopts an iodine-bridged dimeric form (Schmidt et al., 2010). However, a CH···π interaction leads to the formation of chains along the 2_1-axis parallel to *b* (Figure 2). The Zn-I bond length in **1** [2.5198(2) Å] is significantly shorter than that in LZnI [2.615(2) Å], whereas the C-C and C-N bond lengths as well as the N-C-N, C-N-C, and C-C-N bond angles within the amidinate group in **1** and LZnI are almost identical, proving a delocalized π-electron system within the NCN unit of the amidinate ligand. The Zn-N bond length of the coordinated carbodiimide [2.0858(15) Å] is slightly elongated compared to those of the amidinate group [2.0368(14), 2.0589(13) Å] as was expected. The carbodiimide is almost linear [N4-C30-N3 172.74(19)°], and the three-fold coordinated N3 donor atom adopts a trigonal-planar coordination sphere (sum of bond angles 360°). Comparable values were previously reported by Schulz et al. (2008) for [Me(Cl)Zn-N(*i*-Pr)CN*i*-Pr] [N-C-N 358.4°; sum of bond angles 175.4(3)°] and other carbodiimide adducts. In contrast, the carbodiimide units in [Be(*i*-PrNCN*i*-Pr)$_4$](I$_3$)$_2$ largely deviated from linearity (155°), most likely due to the strong polarizing effect of the beryllium ion (Neumüller and Dehnicke, 2010).

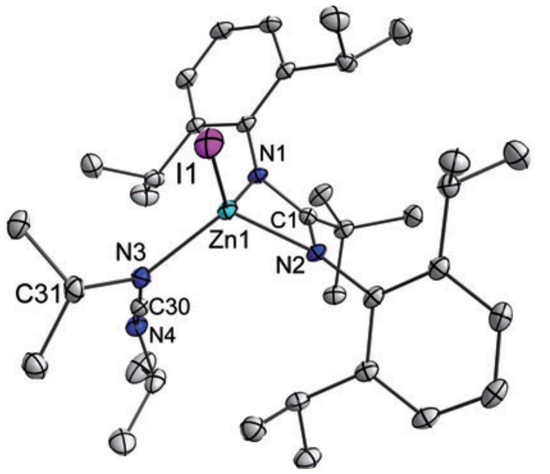


Figure 1 Solid-state structure of **1** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity).
Selected bond lengths (Å) and angles (°): Zn(1)-I(1) 2.5198(2), Zn(1)-N(1) 2.0589(13), Zn(1)-N(2) 2.0368(14), Zn(1)-N(3) 2.0858(15), N(1)-C(1) 1.336(2), N(2)-C(1) 1.346(2), N(3)-C(30) 1.245(2), N(4)-C(30) 1.195(2), N(2)-Zn(1)-N(1) 65.24(5), N(2)-Zn(1)-N(3) 111.54(6), N(1)-Zn(1)-N(3) 109.33(6), N(2)-Zn(1)-I(1) 125.33(4), N(1)-Zn(1)-I(1) 133.57(4), N(3)-Zn(1)-I(1) 106.45(4), C(30)-N(3)-C(31) 118.10(15), C(30)-N(3)-Zn(1) 121.08(12), C(31)-N(3)-Zn(1) 120.82(11), N(4)-C(30)-N(3) 172.74(19).

Homoleptic bis(amidinate) complexes of the type L$_2$Zn [L=RC(NR′)$_2$] have been prepared in the past by reaction of ZnR$_2$ (R=alkyl, amide) with carbodiimides as well as by alkane and salt elimination reactions. Unfortunately, the synthesis of heteroleptic amidinate complexes of the type LZnR is often complicated due to the formation of the corresponding bis(amidinate) complexes. Very recently, Schmidt et al. (2010) reported on the reaction of ZnMe$_2$ with an equimolar amount of amidine LH with elimination, which gave access to the heteroleptic zinc amidinate complex LZnMe. We became further interested to expand this reaction to other starting reagents and report herein on the reaction of Zn[N(SiMe$_3$)$_2$]$_2$ with LH. Zn[N(SiMe$_3$)$_2$]$_2$ was previously reported by Coles and Hitchcock (2004) to react with carbodiimides with insertion into the Zn-N bonds and formation of the corresponding bis(guanidinate) complexes.

Zn[N(SiMe$_3$)$_2$]$_2$ reacts with an equimolar amount of LH with elimination of HN(SiMe$_3$)$_2$ and formation of LZnN(SiMe$_3$)$_2$ **2** in almost quantitative yield. Compound **2** further reacts with (*i*-PrN)$_2$C with insertion of the carbodiimide into the Zn-amide bond and formation of the heteroleptic amidinate-guanidinate complex LZnL′ **3** [L′=(Me$_3$Si)$_2$NC(N*i*-Pr)$_2$] (Scheme 3).

The ^{1}H spectra of **2** and **3** showed resonances due to the amidinate (L) and the amide/guanidinate substituent in the expected 1:1 ratio. Even though single crystals of **3** suitable for an X-ray diffraction study were not obtained, the formation of the homoleptic complexes L$_2$Zn and L$_2$′Zn can be excluded based on the different NMR chemical shifts of **3** compared to those of the homoleptic complexes (Coles and Hitchcock, 2004; Jones et al., 2010).

Single crystals of **2** were obtained from a solution in toluene upon storage at -30°C. Compound **2** crystallizes in the triclinic space group $P\overline{1}$ with two molecules in the asymmetric unit (Figure 3). The two molecules show pseudo-translational symmetry along [110]. However, reducing the cell resulted in a severe disorder of the molecule. Consequently, the initial cell was kept. Figure 4 shows an overlay of the independent molecules to demonstrate the differences in their conformation. The Zn-N [2.040(1), 1.992(1) Å] and C-N bond lengths [1.332(2), 1.339(2) Å] and N-C-N [108.83(10)°] and N-Zn-N bond angles [65.22(4)°] within the amidinate group in **2** are almost identical to those observed for LZnMe and LZnI and **1**, respectively. The values clearly

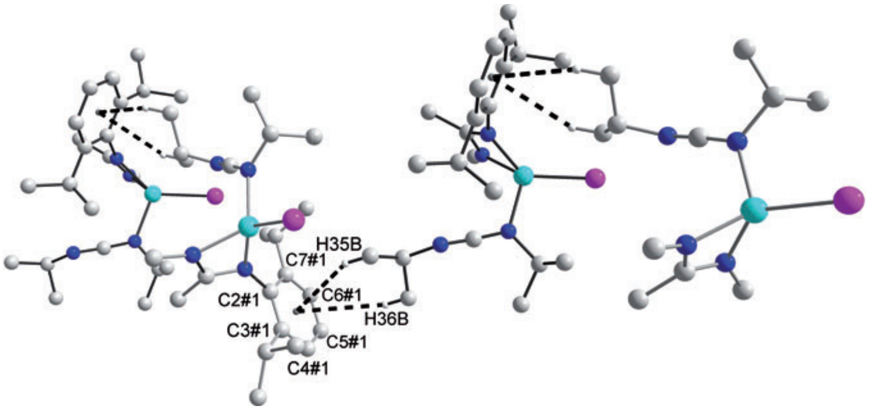


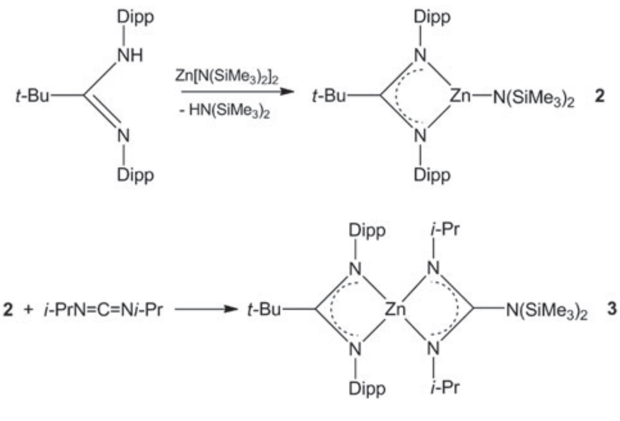
Figure 2 Chains parallel to *b* in the packing of **2** (residual groups are partially omitted for clarity, #1: 2-x, 0.5+y, 1.5-z). C35-H35B···(C2, C3, C4, C5, C6, C7)#1 d(H···centroid) 2.99 Å, <(CH···centroid) 155.4°, <(H···centroid···plane of the ring) 72.8°; C36-H36B···(C2, C3, C4, C5, C6, C7)#1 d(H···centroid) 3.16 Å, <(CH···centroid) 146.8°, <(H···centroid···plane of the ring) 56.6°.

show the formation of a delocalized π-electron system within the NCN unit of the amidinate ligand. The Zn-N_{amide} bond length is significantly shorter compared to the Zn-$N_{amidinate}$ bonds, but agrees well with the values observed by Margraf et al. (2004) for $Zn[N(SiMe_3)_2]_2$ [1.833(11) Å] and other zinc bis(trimethylsilyl)amides as revealed by a Cambridge structural database (CSD) search. The CSD search gave 75 complexes containing a Zn-$N(SiMe_3)_2$ bond. Zn-N bond lengths range from 1.812 to 2.028 Å (av. value 1.914 Å) (CSD, Version 5.33 with update November 2011) (Allen, 2002).

Experimental section

General procedures

All manipulations were performed in a Glovebox (MBraun, München, Germany) under Ar atmosphere or using standard Schlenk line techniques. Dry solvents were obtained from a solvent purification system (MBraun, München, Germany) and degassed prior to use. LH and LZnI (Schmidt et al., 2010) as well as $Zn[N(SiMe_3)_2]_2$ (Bürger et al., 1965) were prepared according to literature method, whereas $(i\text{-PrN})_2C$ (Sigma-Aldrich Chemie GmbH, München, Germany) was commercially available and used as received. ^1H, $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DMX 300 spectrometer (Bruker BioSpin MRI GmbH, Ettlingen, Germany) and are referenced to internal C_6D_5H (^1H: δ=7.154; ^{13}C: δ=128.0). IR spectra were recorded on a Bruker ALPHA-T Fourier transform IR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a single reflection attenuated total reflectance sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Essen (Essen, Germany).



Scheme 3 Synthesis of **2** and **3**.

Synthesis of 1–3

[*t*-BuC(NDipp)$_2$]Zn(I)-N(*i*-Pr)CN*i*-Pr 1 $(i\text{-PrN})_2C$ (1.26 g, 10 mmol) was added via syringe to a solution of $\{[t\text{-BuC(NDipp)}_2]\text{-ZnI}\}_2$ (6.12 g, 5 mmol) in 20 ml of toluene at -30°C. The solution was warmed to ambient temperature and stirred for 2 h, concentrated in vacuum to 10 ml, and stored at 4°C. Colorless crystals of **1** were formed within 12 h.

Yield 7.23 g (98%). Melting point: >220°C. Anal. found (calcd.) for $C_{36}H_{57}IN_4Zn$ (738.13 g/mol): H, 7.8 (7.8); C, 58.6 (58.5); N, 7.6 (7.5). ^1H NMR (300 MHz, C_6D_6, 25°C): δ=0.93 [s, 9H, $C(CH_3)_3$], 0.97 [d, $^3J_{HH}$=6.7 Hz, 12H, $CH(CH_3)_2$], 1.31 [d, $^3J_{HH}$=6.8 Hz, 12H, $CH(CH_3)_2$], 1.34 [d, $^3J_{HH}$=6.8 Hz, 12H, $CH(CH_3)_2$], 3.49 [sept, $^3J_{HH}$=6.8 Hz, 2H, $CH(CH_3)_2$], 3.75 [sept, $^3J_{HH}$=6.8 Hz, 2H, $CH(CH_3)_2$], 7.07 (m, 6H, Ar*H*). ^{13}C NMR (75 MHz, C_6D_6, 25°C): δ=21.4 [$CH(CH_3)_2$], 22.7 [$CH(CH_3)_2$], 23.1 [$CH(CH_3)_2$], 24.2 [$CH(CH_3)_2$], 25.6 [$CH(CH_3)_2$], 27.3 [$CH(CH_3)_2$], 27.8 [$CH(CH_3)_2$], 28.7 [$CH(CH_3)_2$], 29.9 [$CH(CH_3)_2$], 43.9 [$C(CH_3)_3$], 49.6 [$C(CH_3)_3$], 123.0 (Ar-*C*), 127.4 (Ar-*C*), 147.7 (N*C*N), 158.6 (N*C*N). IR: *ν*=2967, 2866, 2139, 1487, 1445, 1432, 1399, 1366, 1300, 1254, 1240, 1212, 1176, 1165, 1131, 1105, 1058, 1044, 962, 934, 916, 896, 803, 763, 729, 715, 639, 579, 463, 433, 408 cm^{-1}.

[*t*-BuC(NDipp)$_2$]ZnN(SiMe$_3$)$_2$ 2 A solution of $Zn[N(SiMe_3)_2]_2$ (1.79 g, 5 mmol) in 10 ml of toluene was added dropwise to *t*-BuC(NHDipp)(NDipp) (2.10 g, 5 mmol) dissolved in 10 ml of toluene at ambient temperature. The resulting solution was stirred for 72 h, concentrated in vacuum to 10 ml, and stored at -30°C. Colorless crystals of **2** were formed within 24 h.

Yield 3.06 g (95%). Melting point: 118°C. Anal. found (calcd.) for $C_{35}H_{61}N_3Si_2Zn$ (645.42 g/mol): H, 9.4 (9.5); C, 64.9 (65.1); N, 6.4

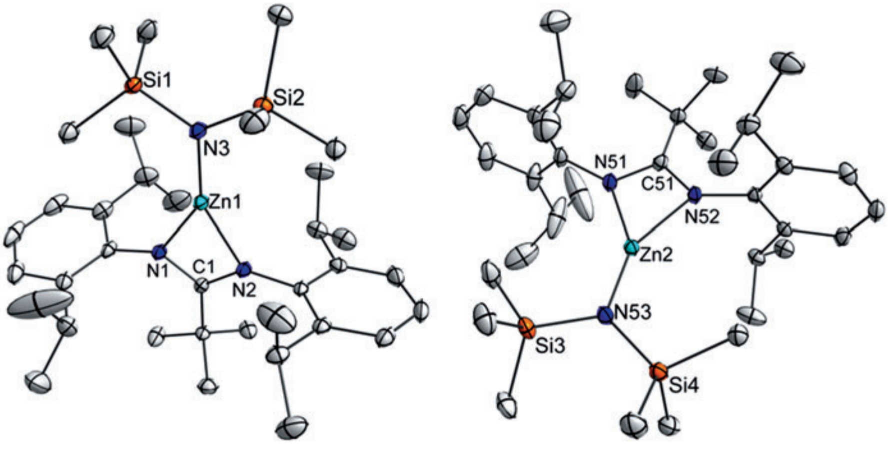


Figure 3 Solid-state structure of **2** (thermal ellipsoids are shown at 50% probability levels; H atoms are omitted for clarity; relative orientation of the molecule does not resemble the arrangement within the asymmetric unit).
Selected bond lengths (Å) and angles (°): Zn(1)-N(3) 1.8512(10), Zn(1)-N(2) 1.9926(10), Zn(1)-N(1) 2.0401(11), Si(1)-N(3) 1.7256(11), Si(2)-N(3) 1.7328(11), N(1)-C(1) 1.3329(15), C(1)-N(2) 1.3399(16), N(3)-Zn(1)-N(2) 149.72(5), N(3)-Zn(1)-N(1) 145.05(4), N(2)-Zn(1)-N(1) 65.22(4), C(1)-N(1)-C(2) 133.54(11), C(1)-N(1)-Zn(1) 92.02(8), C(2)-N(1)-Zn(1) 134.43(8), C(1)-N(2)-C(14) 132.97(10), C(1)-N(2)-Zn(1) 93.92(7), C(14)-N(2)-Zn(1) 132.93(8), N(1)-C(1)-N(2) 108.83(10), Si(1)-N(3)-Si(2) 121.79(6), Si(1)-N(3)-Zn(1) 118.58(6), Si(2)-N(3)-Zn(1) 119.63(6), Zn(2)-N(53) 1.8540(11), Zn(2)-N(52) 2.0027(10), Zn(2)-N(51) 2.0289(11), Si(3)-N(53) 1.7263(11), Si(4)-N(53) 1.7296(12), N(51)-C(51) 1.3396(16), C(51)-N(52) 1.3389(16), N(53)-Zn(2)-N(52) 148.03(5), N(53)-Zn(2)-N(51) 146.36(5), N(52)-Zn(2)-N(51) 65.44(4), C(51)-N(51)-Zn(2) 92.19(8), C(52)-N(51)-Zn(2) 133.40(9), C(51)-N(51)-C(52) 130.02(11), C(51)-N(52)-C(64) 132.82(11), C(51)-N(52)-Zn(2) 93.37(8), C(64)-N(52)-Zn(2) 133.80(8), N(52)-C(51)-N(51) 108.92(11), Si(3)-N(53)-Si(4) 121.71(6), Si(3)-N(53)-Zn(2) 118.46(6), Si(4)-N(53)-Zn(2) 119.67(6).

(6.5). ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ=0.11 [s, 18H, $Si(CH_3)_3$], 0.95 [s, 9H, $C(CH_3)_3$], 1.32 [d, $^3J_{HH}$=6.9 Hz, 12H, $CH(CH_3)_2$], 1.33 [d, $^3J_{HH}$=7.1 Hz, 12H, $CH(CH_3)_2$], 3.59 [sept, $^3J_{HH}$=6.9 Hz, 4H, $CH(CH_3)_2$], 7.06 (m, 6H, Ar*H*). ^{13}C NMR (75 MHz, C_6D_6, 25°C): δ=5.6 [$Si(CH_3)_3$], 22.7 [$CH(CH_3)_2$], 25.3 [$CH(CH_3)_2$], 28.9 [$CH(CH_3)_2$], 30.0 [$CH(CH_3)_2$], 41.7 [$C(CH_3)_3$], 123.7 (Ar-*C*), 125.4 (Ar-*C*), 142.8 (Ar-*C*), 142.9 (Ar-*C*), 180.7 (N*C*N). IR: *ν*=2959, 2871, 2170, 1436, 1403, 1364, 1313, 1246, 1211, 1178, 1095, 1056, 1029, 980, 943, 875, 815, 801, 760, 708, 671, 615, 472 cm^{-1}.

[*t*-BuC(NDipp)$_2$]Zn{(*i*-PrN)$_2$C[N(SiMe$_3$)$_2$]} 3 (*i*-PrN)$_2$C (0.63 g, 5 mmol) was added via syringe to a solution of [*t*-BuC(NDipp)$_2$]-

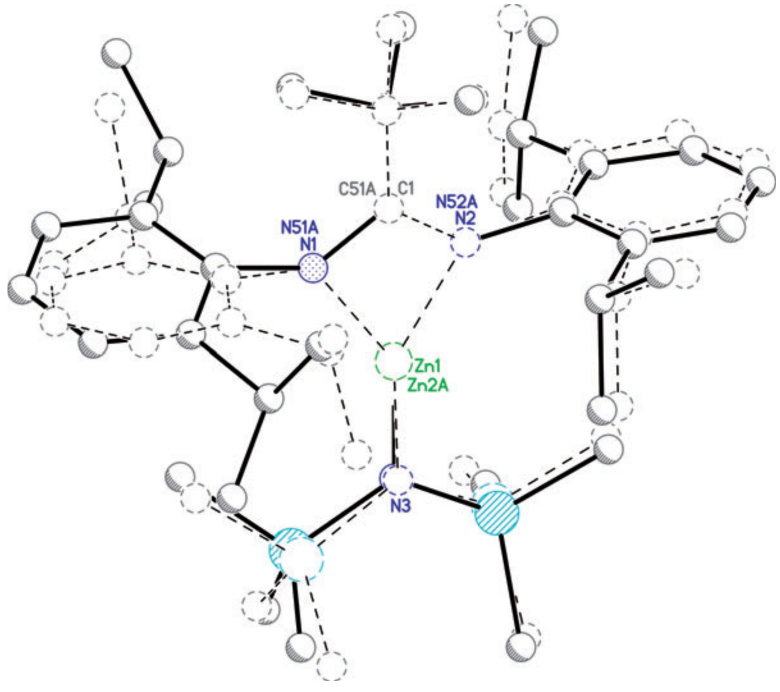


Figure 4 Overlay of the independent molecules of **2** (molecule containing Zn(2) in dashed lines).

Table 1 Crystallographic details of **1** and **2**.

	1	**2**
Empirical formula	$C_{36}H_{57}IN_4Zn$	$C_{35}H_{61}N_3Si_2Zn$
Molecular mass	738.13	645.42
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a (Å)	11.9250(4)	11.4985(2)
b (Å)	15.3035(5)	11.4985(2)
c (Å)	19.8272(7)	19.9837(4)
α (°)	90	80.4660(10)
β (°)	90	86.8710(10)
γ (°)	90	88.7140(10)
V (Å^3)	3618.3(2)	3732.69(12)
Z	4	4
T (K)	100(1)	100(1)
μ (mm^{-1})	1.561	0.748
$D_{calcd.}$ (g cm^{-3})	1.355	1.148
$2\theta_{max}$ (°)	61	58
Crystal size (mm)	0.28×0.17×0.05	0.35×0.33×0.28
Number of reflections	49,879	56,306
Number of unique reflections	10,671	19,824
R_{int}	0.0274	0.0185
Number of parameters refined/restraints	379/0	739/0
Flack-Parameter x	0.001(7)	–
R_1[a]	0.0229	0.0312
wR_2[b]	0.0563	0.0868
Goodness of fit[c]	1.053	1.026
Maximum/Minimum transmission	0.75/0.64	0.75/0.67

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ [for $I>2\sigma(I)$].

[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

[c] Goodness of fit$=\{\Sigma[w(|F_o^2|-|F_c^2|)^2]/(N_{observns}-N_{params})\}^{1/2}$.

$w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$, where $P=(F_o^2+2F_c^2)/3$; a and b are constants chosen by the program.

$ZnN(SiMe_3)_2$ **2** (3.22 g, 5 mmol) in 20 ml of toluene at ambient temperature. The resulting solution was stirred for 12 h at 50°C, concentrated in vacuum to 10 ml, and stored at -30°C. Colorless crystals of **3** were formed within 24 h.

Yield 3.47 g (90%). Melting point: 136°C. Anal. found (calcd.) for $C_{42}H_{75}N_5Si_2Zn$ (771.63 g/mol): H, 9.2 (9.1); C, 65.6 (65.4); N, 9.1 (9.1). ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ=0.32 [s, 18H, $Si(CH_3)_3$], 1.01 [s, 9H, $C(CH_3)_3$], 1.12 [d, $^3J_{HH}$=6.7 Hz, 12H, $CH(CH_3)_2$], 1.39 [d, $^3J_{HH}$=6.5 Hz, 12H, $CH(CH_3)_2$], 1.43 [d, $^3J_{HH}$=6.5 Hz, 12H, $CH(CH_3)_2$], 3.65 [sept, $^3J_{HH}$=6.4 Hz, 2H, $CH(CH_3)_2$], 3.82 [sept, $^3J_{HH}$=6.7 Hz, 4H, $CH(CH_3)_2$], 7.04–7.14 (m, 6H, Ar*H*). ^{13}C NMR (75 MHz, C_6D_6, 25°C): δ=2.4 [$Si(CH_3)_3$], 26.7 [$CH(CH_3)_2$], 28.9 [$CH(CH_3)_2$], 44.3 [$C(CH_3)_3$], 44.7 [$C(CH_3)_3$], 123.3 (Ar-*C*), 165.2 (N*C*N). IR: ν=2965, 2866, 1622, 1585, 1460, 1429, 1375, 1360, 1321, 1230, 1202, 1167, 1141, 1093, 1071, 1019, 944, 895, 797, 756, 728, 686, 660, 619, 528 cm^{-1}.

X-ray crystallography

Crystallographic data for **1** and **2** were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector [Mo-Kα radiation, λ=0.71073 Å; T=100(1) K]. Crystallographic data for **1** and **2** are summarized in Table 1. The structures were solved by Direct Methods (SHELXS-97; Sheldrick, 1997) and refined by full-matrix least squares on F^2. Semi-empirical absorption correction from equivalent reflections on the basis of multiscans (Bruker AXS APEX2) was applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms by a riding model. Despite resolving the pseudo-translational symmetry of **2**, the ADP of C(9, 10, 58, 59) still indicate a severe disorder which could not be resolved. Bond length and angles of these atoms should not be considered reliable. (SHELXL-97; Sheldrick, 1997; see also Sheldrick, 2008; Hübschle et al., 2011).

The crystallographic data of the structures (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-869941 (**1**) and CCDC-869940 (**2**). 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].

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