

Synthesis and Structural Characterization of Monomeric Three-Coordinated β -Diketoiminate Organozinc Derivatives[†]

Jörg Prust, Andreas Stasch, Wenjun Zheng, Herbert W. Roesky,*
Eftichia Alexopoulos, Isabel Usón, Dieter Böhler, and Thomas Schuchardt

Institut für Anorganische Chemie der Universität Göttingen, Tammannstrasse 4,
D-37077 Göttingen, Germany

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Summary: The monomeric zinc compounds with three-coordinated zinc (dipp)NacNacZnCl (**1**), (dipp)NacNacZnMe (**2**), (dipp)NacNacZn^tBu (**3**), and (dipp)NacNacZnPh (**4**) were prepared under mild conditions in strong coordinating donor solvents. Compounds **2–4** have been structurally characterized. The β -diketoiminate ligand (2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)pent-2-ene ((dipp)NacNac) acts as a chelating ligand through its two N atoms, forming a six-membered ring with the zinc atom.

Introduction

Organozinc complexes are extensively used in both organic and organometallic syntheses.^{1,2} In particular, organozinc reagents offer valuable alternatives to the corresponding magnesium and lithium reagents in terms of both their reactivity and selectivity. However, in contrast to dialkylmagnesium reagents, in which the magnesium centers are typically four-coordinated and tetrahedral, dialkylzinc complexes exist as monomeric two-coordinated molecules.³

Although the chemistry of four-coordinated organozinc complexes is well developed, monomeric three-coordinated zinc compounds are still quite rare. Only few examples including [(Me₃Si)₂N(Ph)P(μ -NSiMe₃)₂-ZnPh],⁴ [N{P(NMe₂)₂NSiMe₃}₂ZnN(SiMe₃)₂],⁵ [Et₂ZnC{N(1-Ad)CH₂}₂],⁶ [(Me₃Si)₂N]₂ZnCH₂P(NMe₂)₃],⁷ and [Bp^{Bu}][†][Zn^tBu]⁸ have been reported in the literature.

[†] Dedicated to Professor Rudolf Taube on the occasion of his 70th birthday.

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However, all the known monomeric three-coordinated zinc compounds were synthesized using weakly coordinating solvents such as pentane or toluene. Therefore, application of these compounds will be limited to weakly coordinating solvents; otherwise solvents such as Et₂O or THF will occupy the vacant site at the zinc and decrease the reactivity.

Herein we report the facile synthesis of monomeric compounds with three-coordinated zinc in Et₂O and THF using a bulky β -diketoiminate ligand, 2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)pent-2-ene ((dipp)NacNac).⁹ The other substituents on the zinc atom are chlorine, alkyl, and phenyl groups, respectively. To the best of our knowledge these compounds represent the first monomeric three-coordinated zinc derivatives forming no stable adducts in strong coordinating solvents.

Experimental Section

General Considerations. All experiments were performed using standard Schlenk techniques under a dry nitrogen atmosphere due to the extreme sensitivity of the reactants and products toward air and moisture. A Braun Labmaster 130 drybox was used to store the compounds and to prepare the samples for spectroscopic characterizations. All solvents were dried over sodium/benzophenone, freshly distilled and degassed prior to use. (dipp)NacNacH was prepared as described in the literature.⁹ NMR spectra were recorded on Bruker AM 200 and Bruker AM 250 instruments. Chemical shifts are reported in ppm with reference to tetramethylsilane as external standard. EI mass spectra were obtained on Finnigan MAT 8230 or Varian MAT CH 5 instruments, and FT-IR spectra were measured on a Bio-Rad FTS-7 as Nujol mulls between KBr plates in the range 4000–400 cm⁻¹. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Melting points were measured in sealed glass tubes and are uncorrected.

Preparation of (dipp)NacNacZnCl (1**).** To a suspension of ZnCl₂ (420 mg, 1.55 mmol) in Et₂O (20 mL) was slowly added a solution of (dipp)NacNacLi·OEt₂¹⁰ (3.11 g, 1.55 mmol) in Et₂O (20 mL) at –78 °C. The mixture was allowed to warm to room

(9) [(dipp)NacNacH] has been proved to be a good ligand suitable for main group metals and has led to several interesting results. (a) First monomeric three-coordinated β -diketoiminate magnesium compound was synthesized: Gibson, V. C.; Segal, J. A.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 7120–7121. (b) First monomeric aluminum(I) compound with β -diketoiminate ligand was synthesized: Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem.* **2000**, *112*, 4444–4446; *Angew. Chem., Int. Ed.* **2000**, *39*, 4274–4276.

temperature and then stirred for additional 3 h and filtered. The solution was concentrated to 10 mL. **1** was recrystallized at -24°C to yield a colorless crystalline solid after 2 days (yield 1.48 g, 92%). Mp: 275°C . ^1H NMR (CDCl_3): δ 1.15 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.70 (s, 6 H, CH_3), 3.02 (sept, $J = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 4.87 (s, 1 H, CH), 7.12 (m, 6 H, ArH). ^{13}C NMR (C_6D_6): δ 22.8, 23.3, 25.4, 28.3, 28.8, 94.2, 123.8, 125.2, 141.2, 142.3, 165.4. MS (EI; m/z): 481 ($(\text{M} - \text{Cl})^+$, 41), 516 (M^+ , 100). IR (Nujol mull, cm^{-1}): 1660, 1599, 1261, 1225, 1021, 873, 795, 443. Anal. Calcd for $\text{C}_{29}\text{H}_{41}\text{ClN}_2\text{Zn}$ (518.49): C, 67.18; H, 7.97; N, 5.40. Found: C, 67.0; H, 7.6; N, 5.3. Molecular weight (cryoscopic in THF; g/mol): calcd 518.49; found 505.

Preparation of (dipp)NacNacZnMe (2). (a) ZnMe_2 (2.15 mL of a 2 M solution in toluene, 4.30 mmol) was added to a solution of (dipp)NacNacH (1.80 g, 4.30 mmol) in toluene (20 mL) at 0°C . The mixture was allowed to warm to room temperature and refluxed for 3 days. The pale yellow solution was concentrated (5 mL) and stored overnight at -24°C to afford pale yellow crystals of **2** suitable for X-ray single-crystal structural analysis (yield 1.78 g, 83%).

(b) A solution of MeLi (1.52 mL of a 1.6 M solution in Et_2O , 2.44 mmol) was slowly added to a solution of **1** (1.26 g, 2.44 mmol) in Et_2O (20 mL) at -78°C . The mixture was allowed to warm to room temperature and stirred for 3 h. The mixture was filtered, concentrated (ca. 5 mL), and stored overnight at -24°C to afford pale yellow crystals of **2** suitable for X-ray single-crystal structural analysis (yield 1.15 g, 95%). Mp: 127°C . ^1H NMR (C_6D_6): δ -1.24 (s, 3 H, ZnCH_3), 1.16 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.70 (s, 6 H, CH_3), 3.02 (sept, $J = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 4.89 (s, 1 H, CH), 7.12 (m, 6 H, ArH). ^{13}C NMR (C_6D_6): δ 23.0, 23.2, 24.1, 28.3, 29.1, 95.2, 123.5, 125.7, 141.3, 142.5, 167.3. MS (EI; m/z): 202 (DippNCCCH_3 , 100), 481 ($(\text{M} - \text{Me})^+$, 41), 496 (M^+ , 36). IR (Nujol mull, cm^{-1}): 1658, 1268, 1021, 884, 759, 600, 435. Anal. Calcd for $\text{C}_{30}\text{H}_{44}\text{N}_2\text{Zn}$ (498.05): C, 72.34; H, 8.90; N, 5.62. Found: C, 73.51; H, 9.12; N, 5.80.

Preparation of (dipp)NacNacZn*t*Bu (3). A solution of *t*BuLi (1.17 mL of a 2 M solution in hexane, 2.35 mmol) was slowly added to a solution of **1** (1.21 g, 2.35 mmol) in Et_2O (20 mL) at -78°C . The mixture was allowed to warm to room temperature and stirred for 3 h. The mixture was filtered, concentrated to 5 mL, and stored for 7 days at -24°C to yield a pale yellow solid of **3** (yield 1.16 g, 92%). A solution of **3** in THF affords crystals of **3**(THF) suitable for X-ray single-crystal structural analysis. Mp: 186°C . ^1H NMR (C_6D_6): δ 0.94 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.14 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.75 (s, 6 H, CH_3), 3.24 (sept, $J = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 5.02 (s, 1 H, CH), 7.14 (m, 6 H, ArH). ^{13}C NMR (C_6D_6): δ 22.6, 23.2, 23.6, 23.7, 28.5, 33.3, 95.1, 123.6, 125.7, 141.1, 145.6, 167.3. MS (EI; m/z): 481 ($(\text{M} - \text{tBu})^+$, 100), 538 (M^+ , 6). IR (Nujol mull, cm^{-1}): 1655, 1590, 1554, 1529, 1262, 1239, 1020, 935, 884, 759, 701, 444. Anal. Calcd for $\text{C}_{33}\text{H}_{50}\text{N}_2\text{Zn}$ (540.15): C, 73.38; H, 9.32; N, 5.18. Found: C, 73.6; H, 9.3; N, 5.3.

Preparation of (dipp)NacNacZnPh (4). (a) A solution of PhLi (1.14 mL of a 2 M solution in cyclohexane/ Et_2O , 2.28 mmol) was slowly added to a solution of **1** (1.18 g, 2.28 mmol) in Et_2O (20 mL) at -78°C . The mixture was allowed to warm to room temperature and stirred for 8 h. The mixture was filtered and concentrated to 5 mL and stored for 3 days at -24°C to afford pale yellow crystals of **4** suitable for X-ray single-crystal structural analysis (yield 1.08 g, 85%).

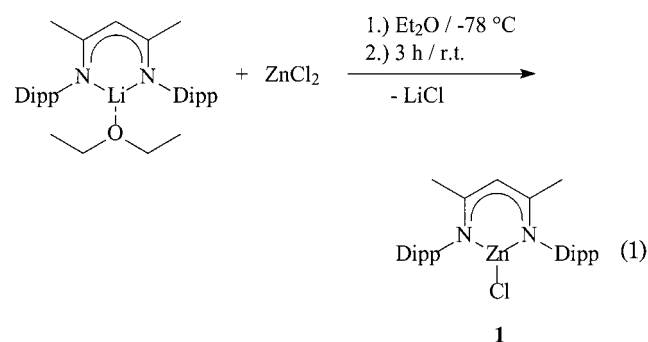
(b) A solution of $\text{Na}[\text{BPh}_4]$ (995 mg, 2.90 mmol) in toluene (20 mL) was slowly added to a suspension of **1** (1.50 g, 2.90 mmol) in toluene (20 mL) at -78°C . The mixture was allowed to warm to room temperature and then stirred for an additional 24 h. The mixture was filtered and concentrated to 10 mL. **4** was recrystallized at -24°C to yield pale yellow crystals of **4** suitable for X-ray single-crystal structural analysis (yield 1.02 g, 63%). Mp: 155°C . ^1H NMR (C_6D_6): δ

1.14 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.21 (d, $J = 6.8$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 1.74 (s, 6 H, CH_3), 3.21 (sept., $J = 6.8$ Hz, 4 H, $\text{CH}(\text{CH}_3)_2$), 5.04 (s, 1 H, CH), 6.83–7.15 (m, 11 H, ArH). ^{13}C NMR (C_6D_6): δ 1.3, 22.6, 23.2, 23.6, 23.7, 28.5, 33.3, 95.1, 123.5, 124.2, 127.8, 127.9, 139.7, 141.7, 145.1, 148.6, 168.0. MS (EI m/z): 417 ((dipp)NacNac, 100), 481 ($(\text{M} - \text{Ph})^+$, 25), 558 (M^+ , 36). IR (Nujol mull, cm^{-1}): 3061, 1623, 1552, 1529, 1262, 1239, 1102, 1024, 935, 884, 757, 721, 701. Anal. Calcd for $\text{C}_{35}\text{H}_{46}\text{N}_2\text{Zn}$ (560.14): C, 75.05; H, 8.28; N, 5.00. Found: C, 75.3; H, 8.7; N, 5.3.

Crystal Structure Solution and Refinement for 2–4. Crystals were mounted on a glass fiber in a rapidly cooled perfluoropolyether.¹¹ Diffraction data of **2** and **4** were collected on a Stoe-Siemens-Huber four-circle-diffractometer coupled to a Siemens CCD area-detector at 133(2) K, with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Diffraction data of **3**(THF) were collected on a Stoe IPDS-II at 133(2) K, with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97)¹² and refined against F^2 on all data by full-matrix least-squares using SHELXL-97.¹³ All hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model if not otherwise stated. The hydrogen atoms on the methyl group at the central β -diketoiminate–backbone–Zn ring in compound **3**(THF) were refined as disordered idealized methyl groups with two half-occupied positions related to each other by rotation of 60° . These hydrogen atoms are allowed to ride on the carbon atoms and rotate about the C(1)–C(3) and C(1A)–C(3A) bond, respectively. Included in the crystal lattice in compound **3** are THF molecules, which do not fulfill the crystallographic symmetry. Their disorder was modeled with the help of similarity restraints for 1,2- and 1,3-distances and rigid bond and similarity restraints on the displacement parameters. The structure parameters and refinement procedures are summarized in Table 1.

Results and Discussion

Synthesis of (dipp)NacNacZnCl (1). Treatment of (dipp)NacNacLi· OEt_2 ¹⁰ with ZnCl_2 in Et_2O gave solvent-free (dipp)NacNacZnCl (**1**) in good yield (eq 1). The EI mass spectrum shows a molecular ion M^+ (m/z 516), which is consistent with monomeric **1**. The formation of **1** is also confirmed by the ^1H NMR spectrum, in which one single resonance for the γ -CH and two doublets for CHMe_2 are observed. No resonances of any Et_2O hydrogen are found (eq 1).



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Table 1. Crystal Data and Structure Refinement for 2, 3(THF), and 4

	2	3(THF)	4
empirical formula	C ₃₀ H ₄₄ N ₂ Zn	C ₃₇ H ₅₈ N ₂ OZn	C ₃₅ H ₄₆ N ₂ Zn
fw	498.04	612.22	560.11
temper [K]	133(2)	133(2)	133(2)
wavelength [Å]	0.71073	0.71073	0.71073
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> 2(1)/ <i>n</i>	<i>Pnma</i>	<i>Pnma</i>
unit cell dimens [Å]	<i>a</i> = 12.482(3) <i>b</i> = 17.053(3) <i>c</i> = 13.961(3) α = 90° β = 104.96(3)° γ = 90°	<i>a</i> = 10.475(2) <i>b</i> = 18.108(4) <i>c</i> = 18.389(4) α = 90° β = 90° γ = 90°	<i>a</i> = 16.850(3) <i>b</i> = 20.727(4) <i>c</i> = 8.9146(18) α = 90° β = 90° γ = 90°
volume [Å ³]	2870.9(10)	3488.2(12)	3113.3(11)
<i>Z</i>	2	4	4
density (calcd) [Mg/m ³]	1.152	1.166	1.195
abs coeff [mm ⁻¹]	0.874	0.733	0.813
<i>F</i> (000)	1072	1328	1200
cryst size [mm ³]	0.70 × 0.40 × 0.10	0.50 × 0.40 × 0.35	0.20 × 0.20 × 0.10
θ range for data collection	2.07 to 27.60°	1.58 to 24.70°	2.42 to 24.71°
no. of reflns collected	50 433	54 534	57 604
no. of ind reflns	6633 [<i>R</i> _{int} = 0.0634]	3071 [<i>R</i> _{int} = 0.0911]	2735 [<i>R</i> _{int} = 0.0656]
refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
no. of data/restraints/params	6633/0/309	3071/54/221	2735/0/183
goodness-of-fit on <i>F</i> ²	1.242	1.043	1.090
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0534 <i>wR</i> 2 = 0.1012	<i>R</i> 1 = 0.0356 <i>wR</i> 2 = 0.0973	<i>R</i> 1 = 0.0396 <i>wR</i> 2 = 0.1023
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0645 <i>wR</i> 2 = 0.1047	<i>R</i> 1 = 0.0382 <i>wR</i> 2 = 0.0991	<i>R</i> 1 = 0.0462 <i>wR</i> 2 = 0.1069
largest diff peak and hole [e·Å ⁻³]	0.360 and -0.759	0.442 and -0.332	0.625 and -0.959

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (dipp)NacNacZnMe (2)

Zn(1)–C(6)	1.941(3)	C(6)–Zn(1)–N(1)	130.21(11)
Zn(1)–N(1)	1.9480(18)	C(6)–Zn(1)–N(2)	132.78(11)
Zn(1)–N(2)	1.9429(18)	N(2)–Zn(1)–N(1)	97.00(8)
N(1)–C(1)	1.329(3)	C(1)–N(1)–Zn(1)	123.64(15)
N(2)–C(3)	1.334(3)	C(3)–N(2)–Zn(1)	122.73(15)
C(1)–C(2)	1.401(3)	N(1)–C(1)–C(2)	123.1(2)
C(2)–C(3)	1.399(3)	N(2)–C(3)–C(2)	124.2(2)

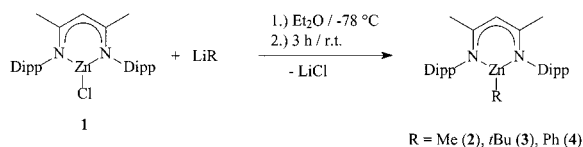
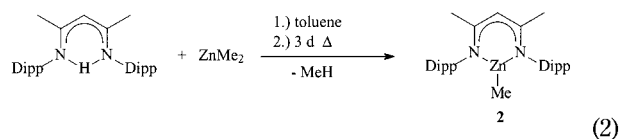
Table 3. Selected Bond Lengths (Å) and Angles (deg) for [(dipp)NacNacZn*t*Bu](THF)

Zn(1)–C(4)	2.009(3)	C(4)–Zn(1)–N(1)	132.52(10)
Zn(1)–N(1)	1.9803(16)	N(1)–Zn(1)–N(1)	94.48(10)
N(1)–C(1)	1.334(3)	C(1)–N(1)–Zn(1)	123.97(13)
C(1)–C(2)	1.400(2)	N(1)–C(1)–C(2)	123.51(19)
		C(1)–C(2)–C(1)	128.9(3)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for (dipp)NacNacZnPh (4)

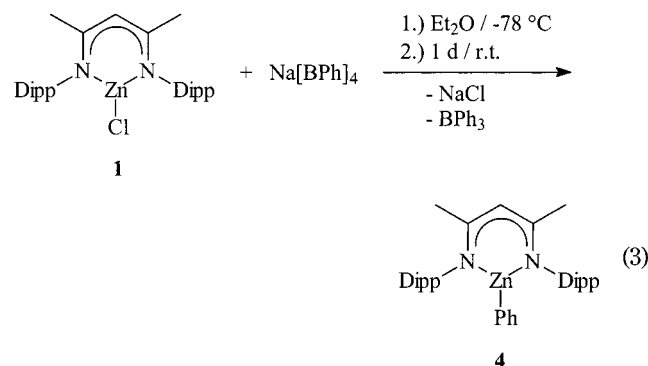
Zn(1)–C(1P)	1.939(3)	C(1P)–Zn(1)–N(1)	131.76(5)
Zn(1)–N(1)	1.9244(18)	N(1)–Zn(1)–N(1)	96.38(11)
N(1)–C(1)	1.325(3)	C(1)–N(1)–Zn(1)	123.88(15)
C(1)–C(2)	1.389(3)	N(1)–C(1)–C(2)	123.5(2)
		C(1)–C(2)–C(1)	128.7(3)

Synthesis of (dipp)NacNacZnMe (2) and (dipp)NacNacZn*t*Bu (3). The reaction of **1** with MeLi (*t*BuLi) in Et₂O (THF) leads to the formation of the solvent-free compounds **2** (**3**) with three-coordinated zinc. Alterna-



tively, **2** can be prepared from the reaction of (dipp)NacNacH with ZnMe₂ in toluene in high yield. The EI mass spectra of **2** and **3** show the molecular ion M⁺ (*m/z* 496 for **2**, 538 for **3**). The ¹H NMR as well as ¹³C NMR spectra are consistent with the formulas given for **2** and **3** (eq 2).

Synthesis of (dipp)NacNacZnPh (4). The reaction of **1** with PhLi in Et₂O proceeded smoothly in the formation of **4** in high yield (eq 2). Alternatively, **4** can be prepared from the reaction of **1** with Na[BPh₄] in toluene. The EI mass spectrum of **4** shows the molecular ion M⁺ (*m/z* 558) and the ¹H NMR as well as ¹³C NMR spectra are consistent with the formula given for **4** (eq 3).



X-ray single-crystal analyses reveal that compounds **2**, **3**(THF), and **4** exhibit some interesting features. Selected bond lengths and angles are listed in Tables 2–4. The central core of the three structures is the (dipp)NacNacZn moiety. The β -diketoiminate ligand (dipp)NacNac acts as a chelating ligand through its two N atoms, forming a six-membered ring with the zinc atom. In compound **2** the Zn–N–C(CH₃)–CH₂–C(CH₃)–N ring is almost planar, whereas in **3**(THF) and

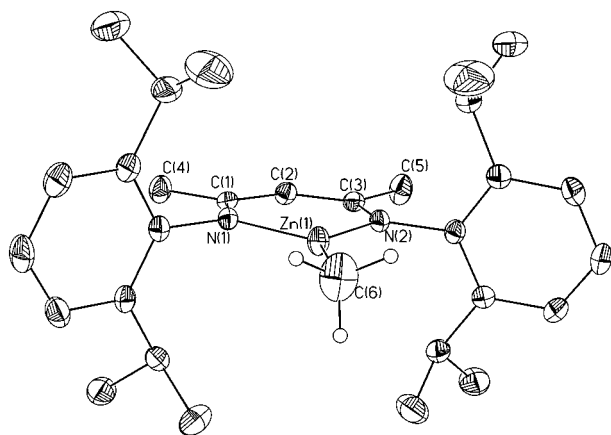


Figure 1. Molecular structure of **2** in the crystal (50% probability). Hydrogen atoms of the β -diketoiminato have been omitted for clarity.

4 it displays a boat conformation with the metal at the prow and the opposite C atom at the stern. The mean deviation from the plane is 0.01 Å (**2**), 0.05 Å (**3**(THF)), and 0.03 Å (**4**). The zinc atom in compound **2** is coordinated by two nitrogen atoms, and one carbon atom completes the planar triangle arrangement (Figure 1). The molecule of **3**(THF) and **4** is generated by a mirror plane. The zinc atom acquires a nearly trigonal planar environment through its coordination to a *t*Bu moiety (**2**) or a phenyl ring (**3**). The distance of the zinc atom to a plane described by N(1)–C(1)–C(4)–C(3)–C(5)–

N(2) in compound **2** is 0.03 Å, whereas in **3**(THF) it is 0.16 Å. The π -electrons of the β -diketoiminato ligand are delocalized since the C(1)–C(2) and the C(2)–C(3) as well as the C(1)–N(1) and the C(3)–N(2) bond lengths in structures **2**, **3**(THF), and **4** are equal within experimental error and correspond to C–C and C–N distances in aromatic systems. Both N–Zn bond lengths are equal as well. The Zn–N (**2**, 1.948(2) and 1.943(2) Å; **3**(THF), 1.980(2) Å; **4**, 1.924(2) Å) distances are shorter than those in comparable Zn–N derivatives.^{8,14} Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit, while compounds **3**(THF) and **4** crystallize in the orthorhombic space group $Pnma$ with half a molecule in the asymmetric unit.

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Supporting Information Available: ORTEP plots and tables of crystal data, refinement details, bond lengths, bond angles, and thermal parameters for **2**, **3**(THF), and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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