

Zinc Complexes with the Chelating Amido-Imino Ligand [1-*n*-Butyl-2-(2,6-diisopropylphenyl)iminoacenaphthen-1-yl]-2,6-diisopropylphenylamide (L): Synthesis, Molecular Structure and Reactivity of [(L)ZnCl]₂, (L)Zn-*n*Bu and (L)ZnN(SiMe₃)₂

Igor L. Fedushkin,^{*,[a]} Alexandra N. Tishkina,^[a] Georgii K. Fukin,^[a] Markus Hummert,^[b] and Herbert Schumann^[b]

Keywords: Zinc / N ligands / Structure elucidation

Dimeric [(L)ZnCl]₂ (**4**) {L = [1-*n*-butyl-2-(2,6-diisopropylphenyl)iminoacenaphthen-1-yl]-2,6-diisopropylphenylamide} was prepared by treatment of the lithium salt of the ligand (LLi) with equimolar amounts of anhydrous ZnCl₂. Treatment of **4** with KN(SiMe₃)₂ affords the bis(trimethylsilyl)amido compound (L)ZnN(SiMe₃)₂ (**5**). The alkylzinc complex (L)Zn-*n*Bu (**6**) is the product of the reaction between the adduct LLi·*n*BuLi (**3**) and ZnCl₂. Compounds **4–6** were characterized by ¹H NMR and IR spectroscopy. The molecular structures of **4** and **6** were determined by single-crystal

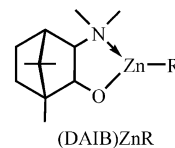
X-ray analysis. In the solid state, the molecules of **4** exist as centrosymmetric, heterochiral dimers bridged by chlorine atoms, while compound **6** consists of monomeric molecules with three-coordinate zinc atoms. The reactions of **6** with *tert*-butanol, adamantanol, 2,5-di-*tert*-butylaniline and diphenylacetonitrile do not proceed with alkane elimination but with protonation of the ligand affording the amino-imine LH (**7**).

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2008)

Introduction

With regard to their chemical behaviour, organozinc compounds resemble organomagnesium and organolithium compounds, but in their addition reactions they are less reactive.^[1] Their lower reactivity towards several functional groups of the respective organic reactants allows the preparation of organozinc compounds that are successfully used in Pd-catalyzed organic cross-coupling reactions.^[2,3] A further synthetic application of zinc organyls is the Noyori addition of R₂Zn compounds to aldehydes mediated by chiral organozinc alcoholates, for example by (DAIB)ZnR. This approach provides a highly enantioselective synthesis of chiral secondary alcohols.^[4]

Over the last few years, monoalkylzinc compounds supported by bi- and tri-dentate N ligands have also been shown to be effective as catalysts for the intramolecular hydroamination of amino olefins^[5] and as syntons for the ring-opening polymerization of lactides.^[6] Except for [(±)-*trans*-Cy(NHSiMe₃)(NSiMe₃)₂Zn₂Et₂]^[6g] all other organo-



DAIB = (2*S*)-3-*exo*-(dimethylamino)isobornoxy
R = Me, Et

zinc catalysts used for the polymerization of lactides are achiral. With regard to this it is worth noting that so far no chiral organozinc derivative has been employed for hydroamination reactions.

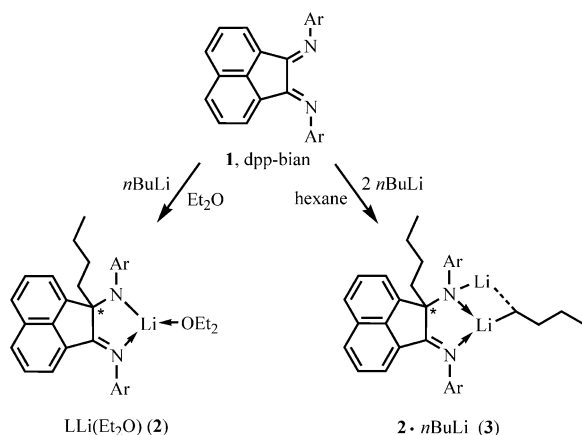
Recently we reported that the reaction between *n*BuLi and 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (**1**, dpp-bian) in diethyl ether produces the lithium salt of the asymmetrically chelating, chiral amido-imino ligand **2**. When the reaction is conducted with the twofold molar amount of *n*BuLi and in the noncoordinating solvent hexane the 1:1 adduct (**3**) of **2** and *n*BuLi is formed (Scheme 1).^[7]

Compound **2** also reacts with GeCl₂ affording the monomeric, three-coordinate germanium(II) compound (L)-GeCl.^[7] As with *n*BuLi, the Grignard reagent EtMgBr adds to the C=N bond of **1** producing the corresponding C-ethylated magnesium product.^[8]

Van Koten and coworkers have shown that the reactions of (2,6-*i*Pr₂C₆H₃)N=CH-CH=N(2,6-*i*Pr₂C₆H₃) (DAB) with dialkylzinc compounds ZnR₂ containing primary or sec-

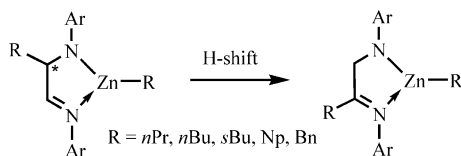
[a] G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina 49, 603950 Nizhny Novgorod, GSP-445, Russia
Fax: +7-831-4627497
E-mail: igorfed@iomc.ras.ru

[b] Institut für Chemie der Technischen Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
Fax: +49-30-31422168
E-mail: schumann@chem.tu-berlin.de



Scheme 1.

ondary alkyl groups ($R = n\text{Pr}$, $n\text{Bu}$, Np , Bn , $s\text{Bu}$) give C -alkylated products that are formed from the initial addition product by a subsequent hydrogen shift from the alkylated carbon to the neighbouring imine carbon atom (Scheme 2). This hydrogen transfer is combined with the loss of chirality of the amido-imino chelating ligand.^[9]



Scheme 2.

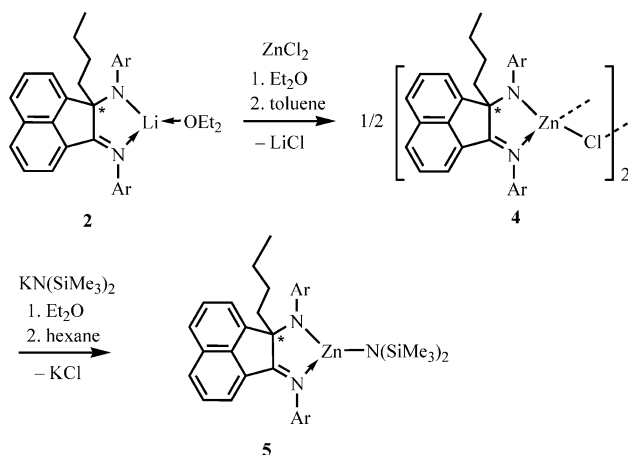
In contrast to the alkylated DAB ligands, the ligand systems formed by the addition of $n\text{BuLi}$ or EtMgBr to **1** are far less labile due firstly to the absence of hydrogen at the respective imino-carbon atom and secondly to the fact that this imino-carbon atom is part of the conformationally rigid cyclic-carbon skeleton.

The reason for our investigations on zinc compounds supported by chelating amido-imino ligands was the suggestion that these compounds might be promising catalysts for both olefin hydroamination and lactide polymerization. In this paper we report on the synthesis, the spectroscopic and chemical properties, and the molecular structure of zinc complexes supported by the amido-imino ligand **L**.

Results and Discussion

Synthesis of $[(\text{L})\text{ZnCl}]_2$ (**4**), $(\text{L})\text{ZnN}(\text{SiMe}_3)_2$ (**5**) and $(\text{L})\text{Zn-}n\text{Bu}$ (**6**) [$\text{L} = [1-n\text{-Butyl-2-(2,6-diisopropylphenyl)-iminoacenaphthen-1-yl]-2,6-diisopropylphenylamide}$]

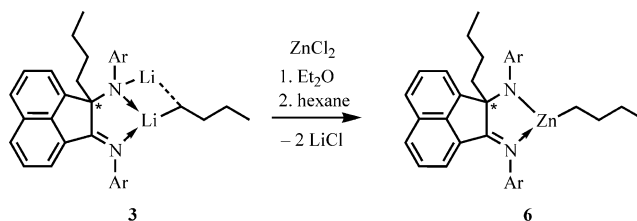
Dimeric $[(\text{L})\text{ZnCl}]_2$ (**4**) is formed by lithium chloride elimination from an equimolar mixture of anhydrous zinc dichloride and the lithium derivative **2** formed by the addition of $n\text{BuLi}$ to dpp-bian (**1**) in diethyl ether. Crystallization from toluene affords red, prismatic crystals of **4** in 70% yield (Scheme 3).



Scheme 3.

Treatment of **4** with $\text{KN}(\text{SiMe}_3)_2$ gives the monomeric bis(trimethylsilyl)amidozinc complex **5**, which can be isolated from hexane as brown crystals in 53% yield. Despite the poor quality of the X-ray data obtained for **5**, the arrangement of the atoms within the molecule could be determined. It corresponds with the picture shown in Scheme 3.

The alkylzinc derivative $(\text{L})\text{Zn-}n\text{Bu}$ (**6**) is the product of the salt elimination reaction between adduct **3** and anhydrous zinc dichloride in diethyl ether (Scheme 4). The adduct **3** precipitates when dpp-bian is reacted with a twofold molar amount of $n\text{BuLi}$ in hexane. The subsequent dissolution of the decanted **3** in diethyl ether may probably cause its splitting into **2** and $n\text{BuLi}$, but, in any case, an exact stoichiometry of the reactants is ensured. Compound **6** crystallizes from hexane as red-orange crystalline needles in 61% yield.



Scheme 4.

Molecular Structures of Compounds **4** and **6**

The molecular structures of **4** and **6** are depicted in Figures 1 and 2, respectively. Each of the two butyl groups in **6** is disordered with regard to two positions. Since there are no significant differences in the geometry of these groups only one orientation of each alkyl chain is shown in Figure 2. The crystal data and structure refinement details for **4** and **6** are given in Table 1, selective bond lengths and angles are listed in Table 2.

The molecular structure of **4** shows centrosymmetric, heterochiral, dimeric molecules ($Z = 2$) formed by two bridging chlorine atoms. Recently, we published the molecular structure of the corresponding heterochiral magnesium

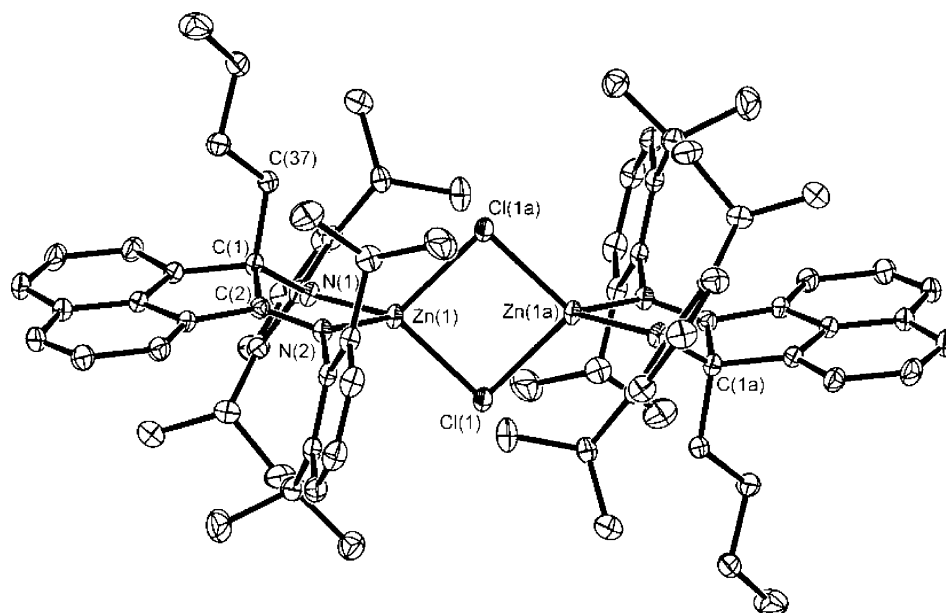


Figure 1. Molecular structure of **4**. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

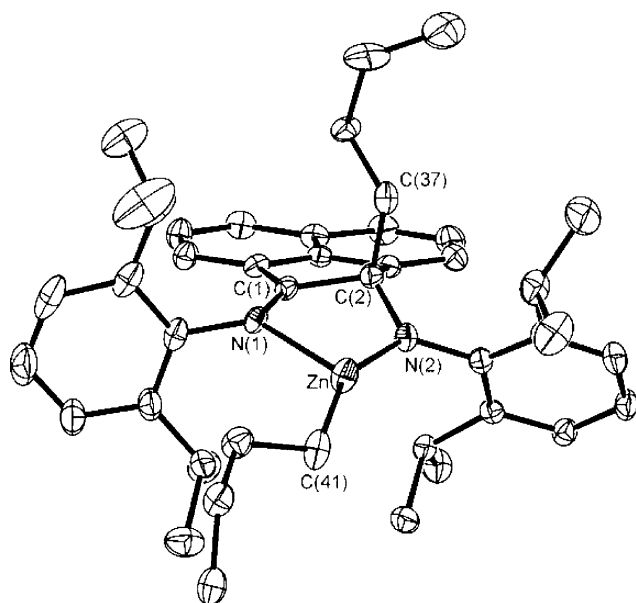


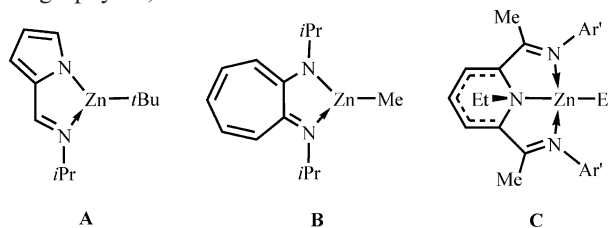
Figure 2. Molecular structure of **6**. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

dimer $[(L')MgCl]_2$ $\{L' = [1-(4\text{-trimethylsiloxybutyl})-2-(2,6\text{-diisopropylphenyl})\text{imino}acena\text{phthen-1-yl}]-2,6\text{-diisopropylphenylamide}\}$ also containing a *C*-alkylated dpp-bian ligand.^[10] The formation and stability of homo- and heterochiral dimers of methylzinc alkoxides has been studied in detail by Noyori and coworkers.^[11] They found that in solution as well as in the solid state, the heterochiral dimers are more stable than the homochiral isomers. The zinc atoms in **4** show a distorted tetrahedral coordination. The significant difference in the length of the metal–halide distances $[Zn(1)–Cl(1) 2.2880(4)$ and $Zn(1)–Cl(1a) 2.4012(4) \text{ \AA}]$ re-

flects the coordinative character of the $Zn(1)–Cl(1a)$ bond. In contrast to compound **4**, molecule **6** represents a three-coordinate monomeric alkylzinc derivative. Although the bond angles $N(1)–Zn(1)–N(2)$ $[83.3(1)^\circ]$, $N(2)–Zn(1)–C(41)$ $[119.4(3)^\circ]$ and $N(1)–Zn(1)–C(41)$ $[153.9(3)^\circ]$ in **6** vary significantly, the sum of the angles (357°) indicates a trigonal-planar environment of the zinc atom. The length of the $Zn–C(nBu)$ bond $[2.006(10) \text{ \AA}]$ compares well with those in $[nBuZnP(SiMe_3)_2]_3$ $[2.035(13), 2.022(16) \text{ \AA}]$.^[12]

The amido-imino character of the chelating *N,N*-ligand in **4** and **6** becomes apparent from the bond length within the fragments $N(1)–C(1)–C(2)–N(2)$ as well as from the zinc–nitrogen bond lengths. The $C(1)–N(1)$ bond lengths in **4** $[1.458(1) \text{ \AA}]$ and **6** $[1.472(5) \text{ \AA}]$ correspond well with the value of carbon–nitrogen single bonds $[1.472(5) \text{ \AA}]$ ^[13] and are significantly longer than the respective $C(2)–N(2)$ bond lengths [**4**: $1.283(1)$; **6**: $1.286(4) \text{ \AA}]$, which are in the range of the lengths of the $C=N$ double bonds in **1** [both $1.282(4) \text{ \AA}]$.^[14] Because of the different functionality of the nitrogen atoms of the *N,N*-ligand, the distances of $N(1)–Zn(1)$ [**4**: $1.897(1)$; **6**: $1.875(3) \text{ \AA}]$ are much shorter than those of $N(2)–Zn(1)$ [**4**: $2.107(1)$; **6**: $2.179(3) \text{ \AA}]$.

Up to now, only three alkylzinc derivatives supported by amido-imino ligands have been characterized by X-ray crystallography: **A**,^[15] **B**^[5a] and **C**.^[16]



The structural parameters of **6** can be compared with those of the three-coordinate Zn species **A** and **B**. In the

Table 1. Crystal data and structure refinement details for **4** and **6**.

	4	6
Empirical formula	C ₄₀ H ₄₉ ClN ₂ Zn·C ₇ H ₈	C ₄₄ H ₅₈ N ₂ Zn
<i>M</i> _r [g mol ^{−1}]	750.77	680.29
Temperature [K]	100(2)	150(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	10.170(5)	10.200(5)
<i>b</i> [Å]	12.554(6)	11.766(5)
<i>c</i> [Å]	16.892(8)	17.028 (5)
α [°]	85.800(10)	85.709(5)
β [°]	81.687(10)	73.545(5)
γ [°]	74.426(10)	79.197(5)
Volume [Å ³]	2054.3(17)	1924.6(14)
<i>Z</i>	2	2
ρ_{calcd} [g cm ^{−3}]	1.214	1.174
μ [mm ^{−1}]	0.696	0.669
<i>F</i> (000)	800	732
Crystal size [mm]	0.25 × 0.22 × 0.14	0.21 × 0.15 × 0.10
$\theta_{\text{min}}/\theta_{\text{max}}$	1.69 to 30.07	2.98 to 27.49
Index ranges	−13 ≤ <i>h</i> ≤ 12 −13 ≤ <i>k</i> ≤ 17 −23 ≤ <i>l</i> ≤ 23	−12 ≤ <i>h</i> ≤ 12 −13 ≤ <i>k</i> ≤ 15 −22 ≤ <i>l</i> ≤ 19
Reflections collected	15564	14390
Independent reflections	10897	7342
<i>R</i> _{int}	0.0146	0.0350
Absorption correction	empirical	empirical
Max./min. transmission	0.9088/0.8451	0.9361/0.8722
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	10897/0/656	7342/20/510
GOF on <i>F</i> ²	1.033	1.158
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.0946	<i>R</i> ₁ = 0.0594, <i>wR</i> ₂ = 0.1534
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.0995	<i>R</i> ₁ = 0.1032, <i>wR</i> ₂ = 0.1716
Largest diff. peak/hole [e Å ^{−3}]	0.851 and −0.297	0.509 and −0.714

Table 2. Selected bond lengths [Å] and angles [°] for **4** and **6**.

	4	6
C(1)–N(1)	1.4583(18)	1.472(5)
C(2)–N(2)	1.2833(18)	1.286(4)
C(1)–C(2)	1.5470(19)	1.536(5)
C(1)–C(37)	1.562(2)	1.63(3)
Zn(1)–N(1)	1.8969(12)	1.875(3)
Zn(1)–N(2)	2.1070(12)	2.179(3)
Zn(1)–C(41)		2.006(10)
Zn(1)–Cl(1)	2.2880(4)	
Zn(1)–Cl(1a)	2.4012(4)	
N(1)–C(1)–C(2)	106.76(11)	108.0(3)
N(2)–C(2)–C(1)	118.87(12)	118.3(3)
N(1)–C(1)–C(37)	112.00(11)	104.5(12)
C(2)–C(1)–C(37)	108.39(12)	110.6(13)
C(1)–N(1)–Zn(1)	109.37(9)	113.9(2)
C(2)–N(2)–Zn(1)	107.09(9)	107.6(2)
N(1)–Zn(1)–N(2)	84.63(5)	83.33(13)
N(1)–Zn(1)–C(41)		153.9(3)
N(2)–Zn(1)–C(41)		119.4(3)
N(1)–Zn(1)–Cl(1)	127.30(4)	
N(1)–Zn(1)–Cl(1a)	125.91(4)	
N(2)–Zn(1)–Cl(1)	122.92(3)	
N(2)–Zn(1)–Cl(1a)	106.08(4)	
Cl(1)–Zn(1)–Cl(1a)	91.385(14)	

troponimate derivative **B** the Zn–N bond lengths are almost equal [1.980(4) and 1.955(4) Å] due to the delocalization of the π electrons over the seven-membered ring and

both N atoms. Although the difference between the Zn–N distances in the pyrrolylaldimine derivative **A** is larger [1.996(5) and 2.089(7) Å] than it is in **B**, it is less pronounced than in **6** [1.875(3) and 2.179(3) Å]. To sum up it can be established that with the increase in the average value of the Zn–N bond lengths on going from **B** (1.967 Å) to **A** (2.043 Å) and **6** (2.027 Å) the Zn–C(alkyl) bond lengths increase in the same order [**B** 1.941(5), **A** 1.990(6), **6** 2.006(10) Å].

¹H NMR Spectroscopy of **4–6**

Selected ¹H NMR spectroscopic data of the compounds **4**, **5** and **6** are presented in Table 3. The asymmetry of the amido-imino ligand of compounds **4–6** causes nonequivalence of all aromatic protons as well as of the four methine protons and the eight methyl groups of the *i*Pr substituents.

In the spectrum of each compound, the methyl groups give rise to the appearance of eight doublets in the range δ = 2 to 0 ppm and the methine protons give rise to four septets in the range δ = 4.8 to 2.6 ppm. The methine proton region in the spectrum of **6** is shown in Figure 3.

The presence of the chiral atom C(1) (see Figures 1 and 2) next to the α -CH₂ group of the ligand-bonded butyl substituent causes the nonequivalence of these two methylene protons and the appearance of two triplets of doublets in

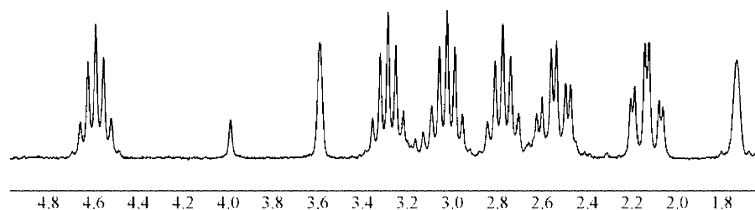


Figure 3. Part of the ^1H NMR spectrum of **6** ($[\text{D}_8]\text{THF}$, 200 MHz, 20 $^\circ\text{C}$).

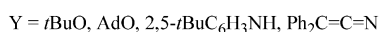
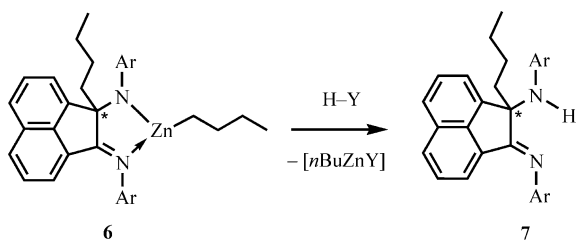
Table 3. Selected ^1H NMR chemical shifts (δ values, ppm) for **4–6** ($[\text{D}_8]\text{THF}$, 200 MHz).

	4	5	6
$(\text{CH}_3)_2\text{HC-Ar}$	4.77	4.58	4.60
	3.38	3.25	3.30
	3.13	3.16	3.04
	2.68	2.66	2.79
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{-C}^*$	2.48	2.79	2.57
	2.34	2.25	2.15

the range $\delta = 3$ to 2 ppm (Table 3). The shift difference of the two diastereotopic protons increase on going from **4** containing four-coordinate zinc to **5** and **6** containing three-coordinate zinc (28, 108, and 84 Hz, respectively). For comparison, in the three-coordinate germylene compound (L)-GeCl, having the same C-alkylated amido-imino ligand, this difference is much larger (300 Hz) and reflects the presence of not only the chiral C(1) but also the chiral Ge atom. In the spectrum of **6** recorded in $[\text{D}_8]\text{THF}$, the resonance of the protons of the $\alpha\text{-CH}_2(n\text{Bu})$ group bonded to the zinc atom appears as a triplet at $\delta = 0.47$ ppm, whereas the spectrum recorded in C_6D_6 shows no signal attributable to these protons. A definite detection of this signal is very difficult because of the overlap of numerous resonances in the range 1.8–0.8 ppm. In the ^1H NMR spectrum of $n\text{Bu}_2\text{Zn}$ recorded in C_6D_6 the respective signal appears at $\delta = 0.40$ ppm.^[17]

Reactivity of **6** Towards Some Organic Substances

In order to synthesize new alkoxy and amido zinc complexes with the alkylated amido-imino ligand L, we treated compound **6** with *tert*-butanol, adamantanol, 2,5-di-*tert*-butylaniline and diphenylacetonitrile. In contrast to our expectations, the reactions of **6** with these substrates do not proceed with elimination of butane, but with protonation of the ligand yielding the amino-imine LH (**7**) (Scheme 5).^[7]



Scheme 5.

Conclusions

The complexes **4–6** are the first zinc chelates containing a chiral amido-imino ligand. They are prepared by simple salt elimination reactions from the lithium salt of the ligand, which in turn can be generated in situ from 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (**1**: dpp-bian) and $n\text{BuLi}$. Unexpectedly, the nucleophilicity of the $n\text{BuZn}$ group in the derivative **6** turned out to be lower than that of the amido ligand. The cancellation of the steric stress within the Zn-metallacycle may be a preliminary explanation of this fact.

Experimental Section

General Remarks: All manipulations were carried out in vacuo using Schlenk techniques. Hexane, diethyl ether and toluene were dried by distillation from sodium/benzophenone. The diimine **1** was prepared by condensation of acenaphthenequinone (Aldrich) with 2,6-diisopropylphenylaniline (Aldrich) in CH_3CN . The solvents $\text{C}_4\text{D}_8\text{O}$ (Aldrich) and C_6D_6 (Aldrich), used for the NMR spectroscopic experiments, were dried with sodium/benzophenone at ambient temperature and were, just prior to use, condensed under vacuum into the NMR tubes already containing the respective compound. Melting points were measured in sealed capillaries. IR spectra were recorded with an FTIR FSM-1201 spectrometer, and ^1H NMR spectra were obtained using a Bruker DPX-200 spectrometer. Complexes **2** and **3** were prepared by literature procedures^[7] and used in situ.

$[(\text{L})\text{ZnCl}]_2$ (4**):** A solution of $n\text{BuLi}$ in hexane (2.74 M, 0.8 mL, 2 mmol) was added to a suspension of **1** (1.00 g, 2 mmol) in Et_2O (20 mL) while stirring. The mixture instantly changed colour from orange to blue. ZnCl_2 (0.27 g, 2 mmol) was then added and the reaction mixture was stirred at 40 $^\circ\text{C}$ for 30 min. Within this time the solution turned red. Evaporation of the solvent and treatment of the residue with toluene (15 mL) caused the precipitation of LiCl formed in the reaction, which was filtered off. Compound **4** (0.92 g, 70%) separated as red crystals from the concentrated clear toluene solution, m.p. 101 $^\circ\text{C}$ (dec.). $\text{C}_{80}\text{H}_{98}\text{Cl}_2\text{N}_4\text{Zn}_2 \cdot 2\text{C}_7\text{H}_8$ (1501.57): calcd. C 75.12, H 7.59; found C 74.96, H 7.35. IR (Nujol): $\tilde{\nu} = 2723$ (w), 1940 (w), 1630 (vs), 1590 (m), 1494 (m), 1431 (vs), 1360 (s), 1347 (w), 1316 (s), 1257 (s), 1205 (m), 1192 (m), 1176 (m), 1160 (w), 1140 (w), 1101 (m), 1081 (w), 1059 (s), 1029 (s), 1007 (w), 995 (w), 963 (w), 934 (w), 917 (m), 860 (m), 833 (m), 804 (s), 783 (vs), 755 (vs), 728 (vs), 693 (m) cm^{-1} . ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$, 20 $^\circ\text{C}$): $\delta = 7.96$ (d, $J = 8.0$ Hz, 1 H, CH arom.), 7.65 (d, $J = 8.3$ Hz, 1 H, CH arom.), 7.43–7.06 (m, 6 H, CH arom.), 6.95 (d, $J = 7.5$ Hz, 1 H, CH arom.), 6.78 (dd, $J = 7.5$, $J = 1.5$ Hz, 1 H, CH arom.), 6.42 (d, $J = 7.0$ Hz, 1 H, CH arom.), 6.17 (d, $J = 7.0$ Hz, 1 H, CH arom.), 4.77 [sept, $J = 7.0$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.38 [sept, $J = 6.8$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$], 3.13 [sept, $J = 6.8$ Hz, 1 H, $\text{CH}(\text{CH}_3)_2$],

(CH₃)₂], 2.55–2.27 [m, 2 H, CH₂(CH₂)₂CH₃], 2.68 [sept, *J* = 6.8 Hz, 1 H, CH(CH₃)₂], 1.46 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 1.35 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 1.26 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 1.23 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 1.15 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 0.85 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 0.62 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], –0.21 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃] ppm.

[(L)ZnN(SiMe₃)₂] (**5**): A solution of *n*BuLi in hexane (2.74 mL, 0.8 mmol) was added to a suspension of **1** (1.00 g, 2 mmol) in Et₂O (20 mL) while stirring. The colour of the mixture instantly changed from orange to blue. After addition of ZnCl₂ (0.27 g, 2 mmol) the mixture was stirred at 40 °C for 30 min. The precipitated LiCl was then filtered off. A solution of KN(SiMe₃)₂ (0.4 g, 2 mmol) in Et₂O (10 mL) was added to the remaining clear solution of **4** that was formed in this reaction, and the mixture was stirred for a few minutes. After evaporation of the solvent in vacuo and dissolution of the residue in hexane (20 mL) the mixture was heated for 30 min at 60 °C, and then filtered off from the precipitated KCl. Concentration of the hexane solution causes the crystallization of compound **5** (0.76 g, 53%) as brown crystals, m.p. 173 °C. IR (Nujol): $\tilde{\nu}$ = 1639 (s), 1615 (w), 1589 (m), 1491 (w), 1463 (s), 1428 (w), 1378 (w), 1363 (s), 1347 (m), 1310 (w), 1254 (m), 1243 (w), 1198 (s), 1190 (w), 1180 (w), 1138 (w), 1109 (m), 1046 (w), 1034 (m), 985 (s), 966 (w), 925 (w), 917 (w), 883 (s), 859 (w), 849 (w), 833 (m), 818 (w), 802 (w), 782 (m), 757 (m), 670 (s), 648 (w), 614 (m) cm^{–1}. ¹H NMR (200 MHz, C₆D₆, 20 °C): δ = 7.36–6.90 (m, 9 H, CH arom.), 6.73 (pst, *J* = 8.0 Hz, 1 H, CH arom.), 6.53 (d, *J* = 7.0 Hz, 1 H, CH arom.), 6.33 (d, *J* = 6.8 Hz, 1 H, CH arom.), 4.75 [sept, *J* = 7.0 Hz, 1 H, CH(CH₃)₂], 3.33 [sept, *J* = 6.8 Hz, 1 H, CH(CH₃)₂], 3.31 [sept, *J* = 6.8 Hz, 1 H, CH(CH₃)₂], 2.93 [td, *J* = 12.5, 1 H, *J* = 4.8 Hz, CH₂(CH₂)₂CH₃], 2.85 [sept, *J* = 6.8 Hz, 1 H, CH(CH₃)₂], 2.41 [td, *J* = 12.5, 1 H, *J* = 3.3 Hz, CH₂(CH₂)₂CH₃], 1.61 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 1.55 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 1.37 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 1.34 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 1.05 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 0.99 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 0.85 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃], 0.60 [t, *J* = 7.4 Hz, 3 H, CH₂(CH₂)₂CH₃], 0.18 [s, 18 H, Si(CH₃)₃], –0.13 [d, *J* = 6.8 Hz, 3 H, CH(CH₃)CH₃] ppm.

[(L)Zn-*n*Bu] (**6**): ZnCl₂ (0.19 g, 1.39 mmol) was added to a solution of compound **3** (0.93 g, 0.7 mmol) in Et₂O (20 mL). The reaction mixture was stirred at 40 °C until the solution turned red-orange. After evaporation of the solvent in vacuo the remaining residue was dissolved in hot hexane (25 mL). The insoluble LiCl was filtered off. Compound **6** was isolated (0.58 g, 61%) as red-orange crystalline needles from the concentrated (7 mL) hexane solution, m.p. 154 °C. C₄₄H₅₈N₂Zn (680.29): calcd. C 77.61, H 8.53; found C 77.47, H 8.30. IR (Nujol): $\tilde{\nu}$ = 2723 (w), 1927 (w), 1638 (s), 1588 (m), 1427 (s), 1361 (m), 1364 (m), 1311 (m), 1254 (s), 1204 (m), 1190 (w), 1160 (w), 1136 (w), 1104 (w), 1059 (m), 1031 (m), 833 (s), 801 (s), 778 (vs), 757 (s), 722 (m) cm^{–1}. ¹H NMR (200 MHz, C₄D₈O, 20 °C): δ = 7.97 (d, *J* = 8.3 Hz, 1 H, CH arom.), 7.67 (d, *J* = 8.3 Hz, 1 H, CH arom.), 7.44–7.22 (m, 6 H, CH arom.), 7.08 (pst, *J* = 7.6 Hz, 1 H, CH arom.), 6.85 (dd., *J* = 7.5, *J* = 1.5 Hz, 1 H, CH arom.), 6.51 (d, *J* = 7.0 Hz, 1 H, CH arom.), 6.09 (d, *J* = 7.0 Hz, 1 H, CH arom.), 4.60 [sept, *J* = 7.0 Hz, 1 H, CH(CH₃)₂], 3.30 [sept, *J* = 7.0 Hz, 1 H, CH(CH₃)₂], 3.04 [sept, *J* = 7.0 Hz, 1 H, CH(CH₃)₂], 2.79 [sept, *J* = 7.0 Hz, 1 H, CH(CH₃)₂], 2.57 [td, *J* = 12.8, *J* = 4.8 Hz, 1 H, CH₂(CH₂)₂CH₃], 2.15 [td, *J* = 12.8, *J* = 3.5 Hz, 1 H, CH₂(CH₂)₂CH₃], 1.49 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 1.37 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 1.25–1.09 [m, 9 H, CH(CH₃)CH₃], 0.80 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 0.69 [d, *J* = 7.0 Hz, 3 H, CH(CH₃)CH₃], 0.69 [t, *J* = 7.3 Hz, 3 H, CH₂(CH₂)₂CH₃], 0.47 [t, *J* = 7.7 Hz, 2 H, CH₂(CH₂)₂CH₃], 0.03 [d, *J*

= 7.0 Hz, 3 H, CH(CH₃)CH₃] ppm. ¹³C NMR (50 MHz, C₄D₈O, 20 °C): δ = 192.8, 150.9, 148.3, 148.2, 143.8, 142.8, 139.9, 138.7, 131.8, 130.2, 128.8, 127.9, 127.0, 125.4, 124.5, 124.4, 124.1, 123.5, 122.7, 79.3, 68.1, 67.7, 66.8, 52.7, 30.8, 30.3, 30.0, 29.3, 29.0, 28.8, 28.1, 26.3, 26.0, 25.6, 25.2, 24.8, 24.6, 24.4, 24.2, 23.9, 20.3, 14.1, 13.9, 8.9 ppm.

Single Crystal X-ray Structure Determination of 4 and 6: The data of **4** were collected with a Siemens SMART CCD diffractometer (graphite-monochromated Mo-*K*_α radiation, ω -scan technique, λ = 0.71073 Å) at 100 K. The data of **6** were collected using an Xcalibur S Sapphire diffractometer (Oxford Diffraction) at 150 K. The structures of **4** and **6** were solved by direct methods using the SHELXS-97^[18] and SIR-2004 programs^[19] respectively, and were refined on *F*² by a full-matrix least-squares method using SHELXL-97.^[20] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions using a riding model. The program SADABS^[21] was used to perform area-detector scaling and absorption corrections.

CCDC-660725 (for **4**) and -660726 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grant no. 07-03-00545 and 06-03-32728), the Alexander von Humboldt Foundation (to I. L. F.), the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft (to H. S.).

- [1] C. Elschenbroich, *Organometallics*, 3rd ed., Wiley-VCH, Weinheim, **2006**, p. 74.
- [2] P. Knochel, N. Millot, A. L. Rodriguez, Ch. E. Tucker, *Preparation and applications of functionalized organozinc compounds*, in *Organic Reactions*, John Wiley & Sons, New York, **2001**, 58, 417–731.
- [3] E. Negishi, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 233–257.
- [4] a) N. Oguni, T. Omi, *Tetrahedron Lett.* **1984**, *25*, 2823–2826; b) R. Noyori, M. Kitamura, *Angew. Chem.* **1991**, *103*, 34–55; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 49–69; c) K. Soai, S. Niwa, *Chem. Rev.* **1992**, *92*, 833–856; d) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, John Wiley & Sons, New York, **1994**; e) M. Yamakawa, R. Noyori, *Organometallics* **1999**, *18*, 128–133.
- [5] a) A. Zulus, M. Dochnahl, D. Hollmann, K. Loehnwitz, J. S. Herrmann, P. W. Roesky, S. Blechert, *Angew. Chem.* **2005**, *117*, 7972–7976; *Angew. Chem. Int. Ed.* **2005**, *44*, 7794–7798; b) M. Dochnahl, J. W. Pissarek, S. Blechert, K. Loehnwitz, P. W. Roesky, *Chem. Commun.* **2006**, 3405–3407; c) N. Meyer, K. Loehnwitz, A. Zulus, P. W. Roesky, M. Dochnahl, S. Blechert, *Organometallics* **2006**, *25*, 3730–3734.
- [6] a) H. R. Kricheldorf, C. Boettcher, *J. Macromol. Sci., Pure Appl. Chem.* **1993**, *A30*, 441–448; b) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 11583–11584; c) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854; d) 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; e) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.* **2002**, *41*, 2785–2794; f) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young Jr, M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2003**, *125*, 11350–11359; g) D. Chakraborty, E. Y.-X. Chen, *Organometallics* **2003**, *22*, 769–774; h) M. P. Coles, P. B. Hitchcock, *Eur. J. Inorg. Chem.* **2004**, 2662–2672; i) M. H. Chisholm,

- J. C. Gallucci, K. Phomphrai, *Inorg. Chem.* **2005**, *44*, 8004–8010; j) J.-C. Wu, B.-H. Huang, M.-L. Hsueh, S.-L. Lai, C.-C. Lin, *Polymer* **2005**, *46*, 9784–9792; k) L. E. Breyfogle, C. K. Williams, V. G. Young Jr, M. A. Hillmyer, W. B. Tolman, *Dalton Trans.* **2006**, 928–936; l) B. Lian, C. M. Thomas, O. L. Casagrande Jr, C. W. Lehmann, T. Roisnel, J. F. Carpentier, *Inorg. Chem.* **2007**, *46*, 328–340.
- [7] I. L. Fedushkin, M. Hummert, H. Schumann, *Eur. J. Inorg. Chem.* **2006**, 3266–3273.
- [8] I. L. Fedushkin, V. M. Makarov, E. C. E. Rosenthal, G. K. Fukin, *Eur. J. Inorg. Chem.* **2006**, 827–832.
- [9] E. Wissing, K. van Gorp, J. Bersma, G. van Koten, *Inorg. Chim. Acta* **1994**, *220*, 55–61.
- [10] I. L. Fedushkin, A. A. Skatova, A. N. Lukoyanov, V. A. Chudakova, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull.* **2004**, *113*, 2751–2762.
- [11] M. Kitamura, M. Yamakawa, H. Oka, S. Suga, R. Noyori, *Chem. Eur. J.* **1996**, *2*, 1173–1181.
- [12] B. Rademacher, W. Schwarz, M. Westerhausen, *Z. Anorg. Allg. Chem.* **1995**, *621*, 287–300.
- [13] R. C. Weast, *Handbook of Chemistry and Physics*, 51st ed., **1970–1971**, p. F155.
- [14] I. L. Fedushkin, V. A. Chudakova, G. K. Fukin, S. Dechert, M. Hummert, H. Schumann, *Russ. Chem. Bull.* **2004**, *53*, 2744–2750.
- [15] J. Lewinski, M. Dranka, I. Kraszevska, W. Sliwinski, I. Justyniak, *Chem. Commun.* **2005**, 4935–4936.
- [16] I. J. Blackmore, V. C. Gibson, P. B. Hitchcock, C. W. Rees, D. J. Williams, A. J. P. White, *J. Am. Chem. Soc.* **2005**, *127*, 6012–6020.
- [17] H. K. Hofstee, J. Boersma, J. D. van der Meulen, G. J. M. van der Kerk, *J. Organomet. Chem.* **1978**, *153*, 245–252.
- [18] G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1990**.
- [19] *SIR2004* M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2005**, *38*, 381.
- [20] G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, **1997**.
- [21] G. M. Sheldrick, *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, Germany, **1996**.

Received: July 26, 2007

Published Online: November 23, 2007