Synthesis and Structural Characterization of β-Diketoiminate Complexes Containing Three-Coordinate Zinc and Copper Atoms

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Dedicated to Professor Dieter Naumann on the occasion of his 60th birthday

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The reaction of the lithium β-diketoiminate complex (dipp)NacNacLi·OEt_2 {(dipp)NacNac = 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-enyl} with $ZnCl_2$ yielded the corresponding (dipp)NacNacZnCl (**1**) and (dipp)NacNacZn(μ-Cl)$_2$Li(OEt_2)$_2$ (**1a**). Treatment of **1** with LiC≡CPh and $NaBH_4$ in diethyl ether gave (dipp)NacNacZnC≡CPh (**2**) and (dipp)NacNacZn(μ-H)$_2$$BH_2$ (**3**). The core element of compounds **1a**–**3** is a six-membered ZnN_2C_3 ring. The structure of **1a** shows the β-diketoiminate backbone in a boat conformation with the tetrahedrally coordinated metal centre in **1a** at the prow and the opposing carbon atom at the stern. The zinc atoms in **2** and **3** show a planar arrangement to the β-diketoiminate plane. The zinc atom in **2** is three-coordinated and that in **3** four-coordinated. Treatment of (dipp)NacNacLi·OEt_2 with CuI in diethyl ether yielded {[Li(OEt_2)][(dipp)NacNacCuI]}$_2$ (**4**). In contrast to **1a**–**3**, compound **4** contains a dimetallic system. The core of compound **4** consists of two six-membered LiN_2C_3 rings and one four-membered Cu_2I_2 ring. In addition to bonds to the two iodine atoms, the three-coordinated copper atom has a further bond to the γ-carbon atom of the six-membered LiN_2C_3 ring.
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Introduction

Recent reports have indicated increasing interest in the β-diketoiminate ligand, due to its sterically demanding and chelating properties.[1,2] Vinamidines are useful for the stabilization of low oxidation states of group-13 elements. Recently, we reported the preparation of (dipp)NacNacAl^I, the first example of a monomeric Al^I compound[3] stable at room temperature. Power et al. described the synthesis of the first compound containing a Ga−N double bond, by using a β-diketoiminate ligand.[4] We have also reported on the synthesis of a β-diketoiminate boranate complex of magnesium, in which the magnesium centre is six-coordinated and octahedral.[5]

While the first metals to have a prominent role in organic synthesis were magnesium and lithium, several of the transition metals have also become very important.[6] Organozinc[7] and organocopper[8] complexes are extensively used in both organic and organometallic synthesis. In particular, these complexes offer valuable alternatives to the corresponding magnesium and lithium reagents. Dialkylzinc complexes exist as monomeric molecules with two-coordinate zinc atoms.[9] However, the corresponding dialkylcopper complexes, such as [$LiCuMe_2$]$_2$, exist as dimers.[10,11] Only discrete R_2Cu^- anions have been observed in crystals in which the lithium cation is complexed by crown ethers.[12] Recent reports have indicated increasing interest in zinc hydrides as reducing agents.[13−15] We have reported the synthesis of [(dipp)NacNacZnH]$_2$ by means of the reaction between [(dipp)NacNacZnF]$_2$ and Et_3SiH.[16]

Although the chemistry of organozinc complexes with four-coordinate zinc atoms has been developed, the synthesis of the corresponding acetylides is not well known. Wright et al. synthesized the first zinc acetylide derivatives in 1996,[17] and Dehnicke et al. have prepared a number of zinc acetylide derivatives.[18,19] Monomeric compounds with three-coordinate zinc are still quite rare; only a few examples have been reported in the literature.[20−27]

Here we report on the formation of a monomeric zinc acetylide complex with a three-coordinate zinc atom. We used the bulky β-diketoiminate 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]pent-2-enyl ligand [(dipp)NacNac]. In summary, we prepared four new β-diketoiminate zinc derivatives − (dipp)NacNacZnCl (**1**), (dipp)NacNacZn(μ-Cl)$_2$Li(OEt_2)$_2$ (**1a**), (dipp)NacNacZnC≡CPh (**2**), and (dipp)NacNacZn(μ-H)$_2$$BH_2$ (**3**) − and also one β-diketoiminate copper derivative, {[Li(OEt_2)][(dipp)NacNacCuI]}$_2$ (**4**).

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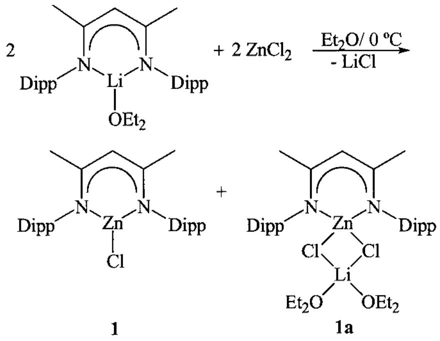
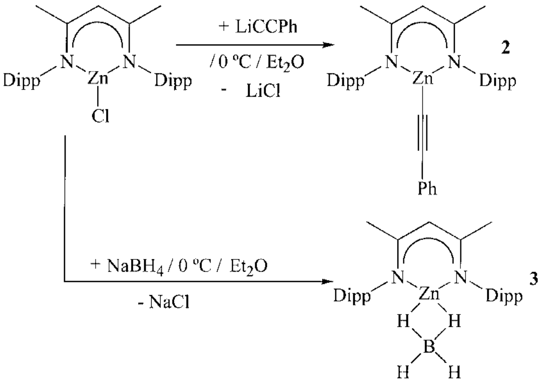
Results and Discussion

Compounds **1** and **1a** were prepared in high yield (92%) by the addition of (dipp)NacNacLi·OEt_2 to a $ZnCl_2$ suspension in diethyl ether (Scheme 1). Compounds **2** and **3** were obtained by addition of LiC≡CPh and $NaBH_4$, respectively, to a solution of **1**. LiCl and NaCl, respectively, were eliminated, and the monomeric zinc complexes **2** and **3** were isolated in high yields (83% **2**, 79% **3**) (Scheme 2).



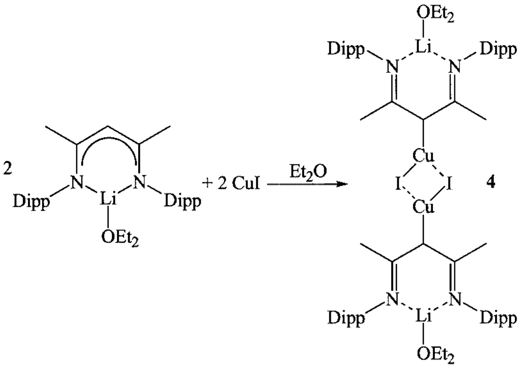
Scheme 1



Scheme 2

Compounds **1**, **2**, and **3** were characterized by EI-MS spectrometry, ^{1}H and ^{13}C NMR and elemental analysis. All compounds are moisture- and air-sensitive. The ^{1}H NMR spectra of **1**, **2**, and **3** showed the typical resonances of the β-diketoiminate unit, with two non-equivalent resonances for the methyl groups of the isopropyl substituents due to the hindered rotation about the Ar−N bonds, as observed for related metal systems.[1−3,28] The ^{1}H NMR spectroscopic data were consistent with the solid-state structures of **2** and **3**. Single crystals suitable for X-ray structural analysis were only obtained for **1a**, but the ^{1}H NMR spectrum was not consistent with the solid-state structure, with no resonances assignable to protons of the diethyl ether molecules being observed. From the predominance of **1** in the NMR and EI-MS spectra (m/z = 516 [M^+]) **1a** is obviously a by-product that crystallises more rapidly than the main product. The EI-MS spectra of **2** and **3**, however, showed the molecular fragments for **2** (m/z = 582 [M^+]) and for **3** (m/z = 482 [$M - BH_3]^+$), respectively.

Reactions with transition metal compounds are widely used in organic chemistry, organocopper compounds being important starting materials for new reactions in synthetic chemistry.[5] Compound **4** was therefore prepared in high yields (76%) by the addition of (dipp)NacNacLi·OEt_2 to a suspension of CuI in diethyl ether at −78 °C (Scheme 3).



Scheme 3

Compound **4** was characterized by EI-MS spectrometry, ^{1}H, ^{13}C, and ^{7}Li NMR and elemental analysis. Like compounds **1**−**3**, compound **4** is air- and moisture-sensitive. The ^{1}H NMR spectrum of **4** showed the typical resonances of the β-diketoiminate unit, the resonances at δ = 0.75 and 2.98 ppm corresponding with the protons of the coordinated ether molecules. The ^{13}C and ^{7}Li NMR spectroscopic data were consistent with the solid-state structure of **4**. The EI-MS showed a fragment of **4** minus one iodine atom (m/z = 1251 [$M - I]^+$).

Because of the similarity of compounds **1**−**7** to β-acetylacetonate complexes, a few examples and their physical properties are listed in Table 1 for comparison.

Table 1. Physical data of compounds **1**−**9**; acac = acetylacetonate, tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne, Tp* = hydrotris(3-cumyl-5-methylpyrazolyl)borate

	M.p. [°C]	^{1}H NMR of γ-C*H* (δ [ppm])
(dipp)NacNacZnCl (**1**)	205	4.88
(dipp)NacNacZnC≡CPh (**2**)	154	5.00
(dipp)NacNacZn(μ-H)$_2$BH$_2$ (**3**)	182−186	4.71
[{Et_2O)Li}{(dipp)NacNacCuI}]$_2$ (**4**)	165	4.24
(dipp)NacNacZnPh (**5**)[2]	155	5.04
(dipp)NacNacMg*i*Pr·Et_2O (**6**)[5]	165	4.85
(dipp)NacNacAl (**7**)[3]	> 150 (dec.)	5.18
(Tp*)Zn(cumoylacetonate) (**8**)[29]	183	5.43
(acac)Cu(tmtch) (**9**)[30]	116	5.37

The compounds **8** and **9** used for the comparison have coordination numbers at their metal centres of three for **8** and of five for **9**. It can be seen that the melting points of the β-acetylacetonate complexes (**8**, **9**) range from 116 to 183 °C, while those of compounds **1**−**4** ranged from 154 to 205 °C. The resonances for γ-CH in **8** and **9** were shifted downfield [δ = 5.43 (**8**), 5.37 (**9**) ppm] relative to the β-diketoiminate compounds **1**−**7**.

Molecular Structures

The central core of compounds **1a**−**3** is a (dipp)NacNacZn unit. The β-diketoiminate ligand acts as a chelating ligand through its two nitrogen atoms, forming a six-membered ring with the zinc atom. The six-membered ZnN_2C_3 ring in **1a** is not planar, but displays a boat conformation with the metal atom at the prow and the opposite carbon atom at the stern, whereas the ZnN_2C_3 rings in **2** and **3** are planar. This deviation from planarity is imposed by the metal centre, as the planar arrangement implies more distortion of its coordination sphere. Nevertheless, the π-electrons of the β-diketoiminate ligand are delocalised, since the C(1)−C(2), C(2)−C(3), C(1)−N(1), and C(3)−N(2) bond lengths in each compound are equal within experimental errors and correspond to those in conjugated systems.[26] Moreover, the two N−Zn bond lengths are equal as well. The Zn−N distances {**1a**: 1.979(2) and 1.982(2) Å; **2** [$(C_7H_8)_{0.5}$]: 1.941(2) and 1.929(2) Å; **3**: 1.917(6) and 1.911(6) Å} are shorter than those in comparable Zn−N derivatives.[28,32−34] The N−Zn−N angles are 97.8° in compound **1a**, 98.8° in **2** and 101.9° in **3**.

The tetrahedral coordination sphere of the zinc atom is completed in compound **1a** by two chlorine atoms and in compound **3** by two hydrogen atoms, whereas the zinc atom in compound **2** adopts a trigonal-planar environment through an additional bond to one C≡CPh moiety.

The central core of **4** is made up of two (dipp)NacNacLi units. As in **1a**−**3**, the β-diketoiminate ligand acts as a chelating ligand through its two nitrogen atoms, forming a six-membered ring with the lithium atom. The LiN_2C_3 rings in **4** are not planar, but display boat conformations with the metal atom at the prow and the opposite γ-carbon atom at the stern. Surprisingly, the copper atom forms a bond to the γ-carbon atom of the β-diketoiminate ligand. In contrast, Tolman et al. recently reported the preparation of a copper(I) compound with the β-diketoiminate ligand in which the copper formed a six-membered CuN_2C_3 ring.[35] A possible explanation for this different behaviour might be that the soft Cu^I prefers coordination with the soft carbon atom while the harder Cu^{II} prefers coordination with the harder nitrogen atoms. The Cu−C bond length of 2.089(6) Å is similar to those found in the literature.[36,37] The trigonal environment of the copper atom is completed by two iodine atoms. The copper atoms form a four-membered Cu_2I_2 ring with the two iodine atoms. The C(1)−C(2) and C(2)−C(3) bond lengths [1.443(8) and 1.455(8) Å] correspond to C−C single bonds, whereas the C−N bond lengths [1.295(8) and 1.299(8) Å] are in the range of C−N double bonds.

The crystallographic data for **1a**, **2**, **3**, and **4** are summarized in Table 6.

Molecular Structure of 1a

Compound **1a** crystallises in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 1). Selected bond lengths and angles for **1** are given in Table 2.

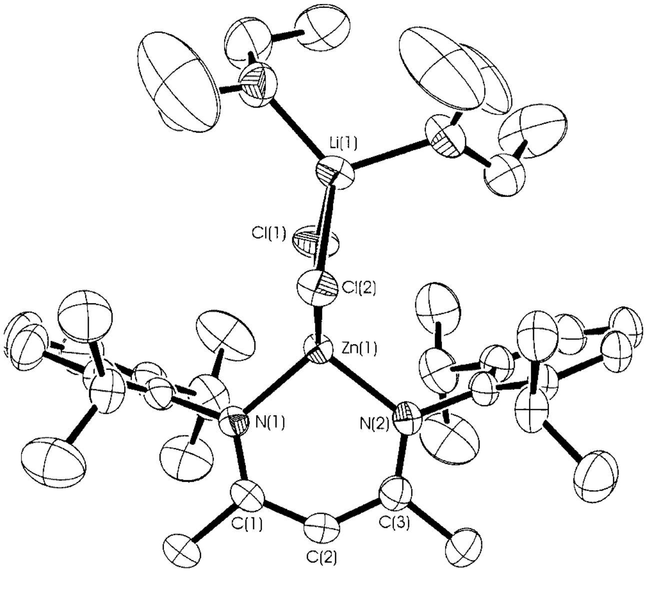


Figure 1. Crystal structure of **1a** (hydrogen atoms are omitted for clarity)

Table 2. Selected bond lengths [Å] and angles [°] of **1a**

Zn(1)−Cl(1)	2.2858(8)	N(1)−Zn(1)−N(2)	97.88(8)
Zn(1)−Cl(2)	2.3144(8)	C(1)−N(1)−Zn(1)	120.42(16)
Zn(1)−N(1)	1.979(2)	C(3)−N(2)−Zn(1)	19.75(17)
Zn(1)−N(2)	1.982(2)	N(1)−C(1)−C(2)	124.0(2)
N(1)−C(1)	1.324(3)	C(3)−C(2)−C(1)	130.1(2)
N(2)−C(3)	1.326(3)	N(2)−C(3)−C(2)	124.3(2)
C(1)−C(2)	1.398(4)	N(1)−Zn(1)−Cl(1)	115.20(6)
C(2)−C(3)	1.409(4)	N(2)−Zn(1)−Cl(1)	117.82(6)
Cl(1)−Li(1)	2.371(5)	N(1)−Zn(1)−Cl(2)	116.71(6)
Cl(2)−Li(1)	2.384(5)	N(2)−Zn(1)−Cl(2)	113.02(6)
		Zn(1)−Cl(1)−Li(1)	84.52(11)
		Zn(1)−Cl(2)−Li(1)	83.63(12)

Molecular Structure of 2

Compound **2** crystallises in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. Besides the two nitrogen atoms of the (dipp)NacNac ligand, the zinc atom coordinates to one phenylacetylide group, a trigonal coordination sphere of the zinc atom thus being formed (Figure 2). Furthermore, the Zn−C≡C backbone deviates from linearity [Zn−C(30)−C(31): 168.18(19)°]. This deviation from linearity has been reported for corresponding transition metal complexes[32−34] and also found in aluminium compounds.[38] Selected bond lengths and angles for **2** are given in Table 3.

Molecular Structure of 3

Compound **3** crystallises in the monoclinic space group $P2_1/n$ (Figure 3). The B−H(b1 and b2) bond lengths are nearly equal [1.211(8) and 1.214(8) Å]. Compound **3** is thus a boranate complex but not an adduct of BH_3. The terminal B−H bond lengths correspond to those found in the literature.[13−15] Selected bond lengths and angles for **3** are given in Table 4.

Molecular Structure of 4

Compound **4** crystallises in the monoclinic space group $P2_1/n$ with half a molecule in the unit cell (Figure 4). Selected bond lengths and angles for **4** are given in Table 5.

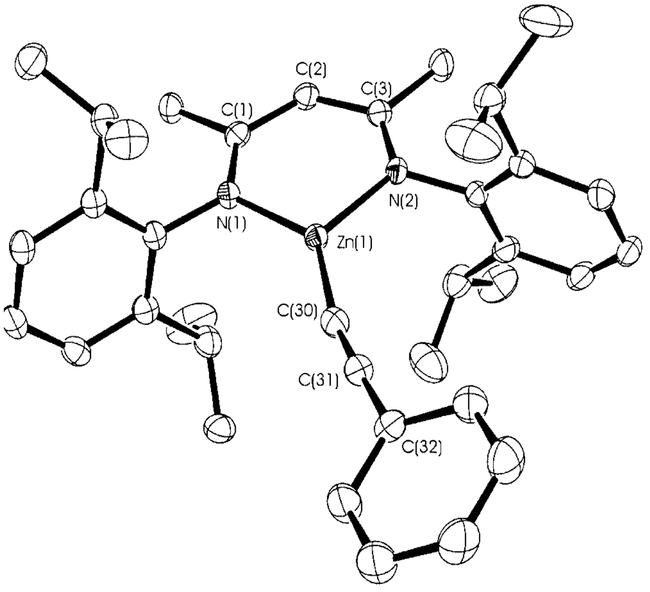


Figure 2. Crystal structure of **2** (hydrogen atoms are omitted for clarity)

Table 3. Selected bond lengths [Å] and angles [°] of **2**

Zn(1)−C(30)	1.906(2)	Zn(1)−C(30)−C(31)	168.18(19)
Zn(1)−N(1)	1.941(2)	C(30)−C(31)−C(32)	177.1(2)
Zn(1)−N(2)	1.929(2)	N(1)−Zn(1)−N(2)	98.85(7)
N(1)−C(1)	1.333(3)	N(1)−Zn(1)−C(30)	124.14(8)
N(2)−C(3)	1.335(3)	N(2)−Zn(1)−C(30)	137.01(8)
C(1)−C(2)	1.403(3)	N(1)−C(1)−C(2)	123.55(18)
C(2)−C(3)	1.406(3)	N(2)−C(3)−C(2)	123.87(19)
C(30)−C(31)	1.207(3)	C(3)−C(2)−C(1)	129.56(19)
C(31)−C(32)	1.439(3)		

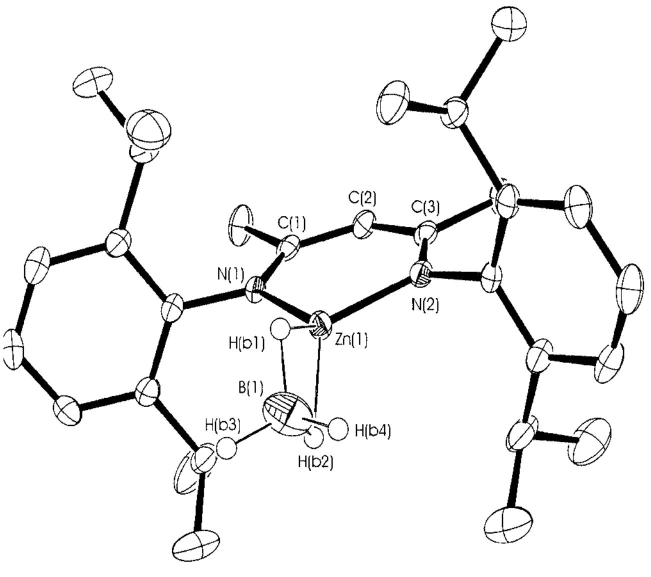


Figure 3. Crystal structure of **3** (hydrogen atoms are omitted for clarity)

Table 4. Selected bond lengths [Å] and angles[°] of **3**

Zn(1)−N(1)	1.917(6)	N(1)−Zn(1)−N(2)	101.96(3)
Zn(1)−N(2)	1.911(6)	B(1)−H(b1)−Zn(1)	91.08(7)
Zn(1)−H(b1)	1.754(9)	B(1)−H(b2)−Zn(1)	91.47(7)
Zn(1)−H(b2)	1.744(9)	H(b1)−Zn(1)−N(1)	120.91(12)
B(1)−H(b1)	1.211(8)	H(b1)−Zn(1)−N(2)	123.50(12)
B(1)−H(b2)	1.214(8)	H(b2)−Zn(1)−N(1)	119.80(12)
B(1)−H(b3)	1.059(8)	H(b2)−Zn(1)−N(2)	121.03(12)
B(1)−H(b4)	1.052(8)	Zn(1)−N(1)−C(1)	119.48(6)
N(1)−C(1)	1.333(4)	Zn(1)−N(1)−C(3)	119.78(6)
N(2)−C(3)	1.334(4)	N(1)−C(1)−C(2)	124.21(4)
C(1)−C(2)	1.394(3)	C(1)−C(2)−C(3)	130.66(4)
C(2)−C(3)	1.404(3)		

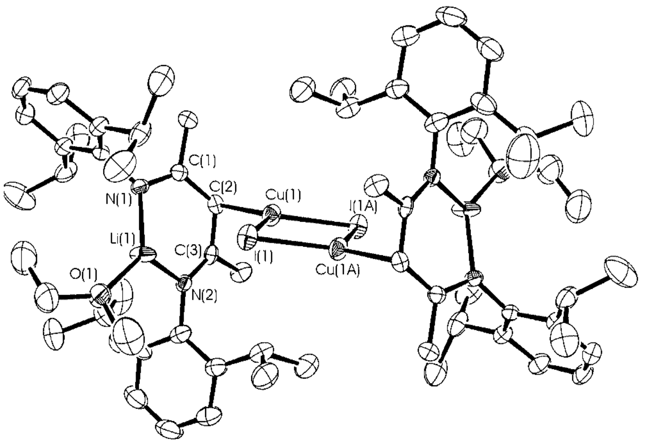


Figure 4. Crystal structure of **4** (hydrogen atoms are omitted for clarity)

Table 5. Selected bond lengths [Å] and angles [°] of **4**

Cu(1)−C(2)	2.089(6)	C(2)−Cu(1)−I(1)	117.4(2)
Cu(1)−I(1)	2.5711(2)	C(1)−C(2)−Cu(1)	91.8(3)
N(1)−Li(1)	1.969(10)	C(3)−C(2)−Cu(1)	110.8(4)
N(2)−Li[(1)	1.973(11)	C(1)−N(1)−Li(1)	117.5(5)
N(1)−C(1)	1.295(8)	C(3)−N(2)−Li(1)	117.5(5)
N(2)−C(3)	1.299(8)	C(3)−N(2)−Li(1)	114.9(5)
C(1)−C(2)	1.443(8)	N(1)−C(3)−C(2)	123.3(5)
C(2)−C(3)	1.455(8)	N(2)−C(3)−C(2)	124.4(5)

Conclusions

The sterically demanding β-diketoiminate ligand (dipp)NacNac facilitates the stabilization of compounds with low-coordination sites at the metal centre. We have synthesized three zinc β-diketoiminate complexes and one copper β-diketoiminate complex with novel structural motifs generated through substitution of the chlorine and iodine atom, respectively. We are at present investigating these compounds as alternatives for Grignard reagents in organic syntheses.

Experimental Section

General: All reactions were performed by standard Schlenk and dry-box techniques. Solvents were appropriately dried and distilled under dinitrogen prior to use. All NMR spectra were recorded in 5-mm tubes with dry degassed [D$_6$]benzene as a solvent, referenced externally to SiMe$_4$. Elemental analyses were performed by the Analytisches Chemisches Laboratorium des Instituts für Anorganische Chemie, Göttingen, and (dipp)NacNacH and (dipp)NacNacLi·OEt$_2$ were prepared by literature procedures.[3]

(dipp)NacNacZnCl (1): A solution of (dipp)NacNacLi·OEt$_2$ (3.11 g, 1.55 mmol) in Et$_2$O (20 mL) was slowly added at −78 °C to a suspension of ZnCl$_2$ (420 mg, 1.55 mmol) in Et$_2$O (20 mL). The mixture was allowed to warm to room temperature and then stirred for an additional 3 h and filtered. The solution was reduced in vacuo to 10 mL and stored at −24 °C to yield **1** and **1a** [(dipp)NacNacZn(μ-Cl)$_2$LiOEt)$_2$]$_2$ as colourless crystalline solids after 2 d. Data for **1**: Yield 1.48 g, 92%. M.p. 205 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 1.15 [d, J = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.16 [d, J = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.18 [d, J = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.20 [d, J = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.70 (s, 6 H, CH_3), 1.75 (s, 6 H, CH_3), 3.02 (sept, J = 6.8 Hz, 3.07 [sept, J = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 4.87 (s, 1 H, CH), 4.89 (s, 1 H, CH), 7.12 (m, 6 H, ArH) ppm. ^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 23.3 [NC(CH$_3$)], 25.4 [CH(CH$_3$)$_2$], 28.8 [CH(CH$_3$)$_2$], 94.2 (γ-C), 123.8 (ArC), 125.2 (ArC), 141.2 (ArC), 142.3 (ArC), 165.4 (NC) ppm. MS (EI): m/z (%) = 481 (21) [M − Cl]$^+$, 516 (100) [M$^+$]. C$_{29}$H$_{41}$ClN$_2$Zn (518.49): calcd. C 67.18, H 7.97, N 5.40; found C 67.0, H 7.6, N 5.3. Molecular mass (cryoscopic in THF in g/mol): calcd. 518.49; found 505. Only single crystals of **1a** were suitable for X-ray structural analysis.

(dipp)NacNacZnC≡CPh (2): A solution of LiC≡CPh (2.34 mL of a 1.0 M solution in THF, 2.34 mmol) was slowly added at −78 °C to a stirred solution of (dipp)NacNacZnCl (1.21 g, 2.34 mmol) in Et$_2$O (20 mL). The reaction mixture was stirred for an additional 3 h and allowed to warm to room temperature. The residue was filtered and the solution was concentrated to 10 mL under reduced pressure. Storage at −24 °C afforded colourless crystals of **2**: Yield 1.13 g (1.94 mmol), 83%. M.p. 154 °C. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ = 1.17 [d, J = 6.8 Hz, 12 H, CH(CH_3)$_2$], 1.40 [d, J = 6.8 Hz,12 H, CH(CH_3)$_2$], 1.67 (s, 6 H, CH_3), 3.19 [sept, J = 6.8 Hz, 4 H, CH(CH$_3$)$_2$], 5.00 (s, 1 H, CH), 6.72−7.28 (m, 11 H, ArH) ppm. ^{13}C NMR (125 MHz, C$_6$D$_6$): δ = 20.5 [NC(CH$_3$)], 23.7 [CH(CH$_3$)$_2$], 24.5 CH(CH$_3$)$_2$, 28.3 [CH(CH$_3$)$_2$], 77.7 (C≡C), 83.8 (C≡C), 94.3 (γ-C), 123.3 (ArC), 123.5 (ArC), 124.5 (ArC), 125.1 (ArC), 128.2 (ArC), 139.2 (ArC), 142.6 (ArC), 161.9 (NC) ppm. MS (EI): m/z (%) = 202 (100) [DippNCCH$_3$], 481 (29) [M − C≡CPh]$^+$, 582 (59) [M$^+$]. C$_{37}$H$_{46}$N$_2$Zn (584.16): calcd. C 76.08, H 7.94, N 4.80; found C 75.5, H 7.94, N 4.6.

(dipp)NacNacZn(μ-H)$_2$BH$_2$ (3): A solution of (dipp)NacNacZnCl (1.59 g, 3.10 mmol) in Et$_2$O (20 mL) was slowly added at −78 °C to a suspension of NaBH$_4$ (0.117 g, 3.10 mmol) in Et$_2$O (10 mL).

Table 6. Crystallographic data of **1a**, **2**, **3**, and **4**

	1a	**2**·(C$_7$H$_8$)$_{0.5}$	**3**	**4**
Empirical formula	C$_{37}$H$_{61}$Cl$_2$LiN$_2$O$_2$Zn	C$_{40.5}$H$_{54}$N$_2$Zn	C$_{29}$H$_{45}$BN$_2$Zn	C$_{66}$H$_{102}$Cu$_2$I$_2$Li$_2$N$_4$O$_2$
Formula mass	709.09	634.23	497.85	1378.28
Temperature [K]	203	133(2)	133(2)	203(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions	a = 12.0841(17) Å b = 21.2125(5) Å c = 15.896(3) Å β = 99.961(16)°	a = 18.0736(6) Å b = 19.2773(9) Å c = 21.1298(8) Å β = 104.969°	a = 12.344(3) Å b = 17.605(4) Å c = 13.884(3) Å β = 104.93(3)	a = 10.622(3) Å b = 26.509(16) Å c = 12.542(3) Å β = 107.77(2)°
Volume [Å^3]	6031(13)	7112.0(5)	2914.4(10)	3363.0(23)
Z	4	8	4	2
Density (calculated) [Mg/m^3]	1.168	1.185	1.135	1.361
Absorption coefficient [mm^{-1}]	0.772	0.720	0.860	1.593
F(000)	1520	2728	1072	1424
Crystal size [mm]	0.8 × 0.6 × 0.3	0.4 × 0.3 × 0.4	0.2 × 0.2 × 0.1	0.8 × 0.6 × 0.3
θ range for data collection	3.55 to 25.00°	1.57 to 24.79°	2.06 to 24.44°	3.52 to 24.99°
Reflections collected	9210	53140	35772	5885
Independent reflections	7073 [R_{int} = 0.0547]	6097 [R_{int} = 0.0489]	4800 [R_{int} = 0.1107]	5874 [R_{int} = 0.0474]
Data/restraints/parameters	7073/0/420	6097/0/417	4800/3/324	5868/0/364
Goodness-of-fit on F^2	1.039	1.077	1.027	1.166
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0488 $wR2$ = 0.1380	$R1$ =0.0344 $wR2$ = 0.1091	$R1$ = 0.0446 $wR2$ = 0.1097	$R1$ = 0.0594 $WR2$ = 0.1682
R indices (all data)	$R1$ = 0.0551 $wR2$ = 0.1380	$R1$ = 0.0380 $wR2$ = 0.1108	$R1$ = 0.0578 $wR2$ = 0.1189	$R1$ = 0.0652 $WR2$ = 0.1762
Largest diff. peak and hole [e·Å^{-3}]	0.979 and −1.066	1.127 and −0.346	0.288 and −0.448	0.954 to −1.089

The mixture was allowed to warm to room temperature and then stirred for an additional 12 h and filtered. The solution was reduced to 5 mL in vacuo and stored at −24 °C to yield colourless crystals of **3**: Yield 1.21 g, 79%. M.p. 182−186 °C. ^{1}H NMR (500 MHz, C_6D_6): δ = 1.15 [d, J = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.19 [d, J = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.59 (s, 6 H CH_3), 3.48 [sept, J = 6.8 Hz, 4 H, $CH(CH_3)_2$], 4.71 (s, 1 H, C*H*), 7.12−7.19 (m, 6 H, Ar*H*) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 23.1 [NC(CH_3)], 24.7 [CH(CH_3)$_2$], 25.2 [CH(CH_3)$_2$], 28.6 [*C*H(CH_3)$_2$], 97.9 (γ-*C*), 124.8 (Ar*C*), 125.1 (Ar*C*), 142.1 (Ar*C*), 168.1 (N*C*) ppm. MS (EI): *m*/*z* (%) = 417 (100) $[M - ZnBH_4]^+$, 482 (43) $[M - BH_3]^+$. $C_{29}H_{45}BN_2Zn$ (497.85): calcd. C 69.96, H 9.12, N 5.63; found C 68.2, H 7.9, N 4.8.

[{Et_2O)Li}{(dipp)NacNacCuI}]$_2$ (4): A solution of (dipp)NacNacLi·OEt_2 (1.18 g, 2.28 mmol) in Et_2O (20 mL) was slowly added at −78 °C to a suspension of CuI (434 mg, 2.28 mmol) in Et_2O (20 mL). The mixture was allowed to warm to room temperature and then stirred for an additional 24 h and filtered. The solution was concentrated to 5 mL under reduced pressure. Storage at −24 °C afforded colourless crystals of **4**. Yield 1.19 g, 76%. M.p. 165 °C (decomp.). ^{1}H NMR (500 MHz, C_6D_6): δ = 0.75 (t, J = 6.8 Hz, 12 H, OCH_2CH_3), 1.12 [d, J = 6.8 Hz, 24 H, $CH(CH_3)_2$], 1.21 [d, J = 6.8 Hz, 24 H, $CH(CH_3)_2$], 1.78 (s, 12 H, CH_3), 2.98 (q, J = 6.8 Hz, 8 H, OCH_2CH_3), 3.13 [sept, J = 6.8 Hz, 4 H, $CH(CH_3)_2$], 4.24 (s, 2 H, C*H*), 7.08−7.14(m, 12 H, Ar*H*) ppm. ^{7}Li NMR (97 MHz, C_6D_6): δ = 0.64 ppm. ^{13}C NMR (C_6D_6): δ = 14.6 (CH_3CH_2O), 23.3 [NC(CH)$_3$], 24.0 [CH(CH_3)$_2$], 24.4 [CH(CH_3)$_2$], 28.1 [*C*H(CH_3)$_2$], 64.3 (γ-*C*), 124.1 (Ar*C*), 125.3 (Ar*C*), 141.9 (Ar*C*), 144.8 (Ar*C*), 163.5 (N*C*) ppm. MS (EI): *m*/*z* (%) = 202 (100) [DippNCCH$_3$], 417 (30) [(dipp)$_2$NacNac], 1251 (40) $[M - I]^+$. $C_{66}H_{102}Cu_2I_2Li_2N_4O_2$ (1378.28): calcd. C 57.51, H 7.46, N 4.06; found C 58.7, H 8.5, N 5.2.

Crystal Structure Determination: All crystals were mounted on glass fibres in a rapidly cooled perfluoropolyether.[39] Diffraction data for **1a** and **4** were collected with a Stoe-Siemens-Huber four-circle diffractometer at 203(2) K, with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), while diffraction data for **2** and **3** were collected with a Stoe IPDS-II at 133(2) K, again with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97 and refined against F^2 on all data by full-matrix, least squares with SHELXS-97.[40,41] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the model at geometrically calculated positions and refined with a riding model if not otherwise stated (Table 6). Atomic coordinates, thermal parameters, bond lengths and angles: CCDC-175030 (**1a**), -175031 (**2**), 175033-(**3**), and -175032 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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