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Binuclear Zinc Complexes with Radical-Anionic Diimine Ligands

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The reactions of (dpp-BIAN)Zn–Zn(dpp-BIAN) (**1**) with PhC≡CH and of [(dpp-BIAN)–Zn(μ-I)]₂ (**2**) with potassium hydride yield the binuclear complexes [(dpp-BIAN)Zn(μ-C≡CPh)]₂ (**3**) and [(dpp-BIAN)Zn(μ-H)]₂ (**4**), respectively (dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene). Complex **3** is also obtained by thermal dehydrogenation of [dpp-BIAN(H)]Zn–(C≡CPh) (**5**), which in turn can be prepared by reacting ZnI₂ with equimolar amounts of [dpp-BIAN–(H)]Na and PhC≡CNa. The paramagnetic compounds **3** and **4** have been characterized by ESR spectroscopy; the diamagnetic complex **5**, by ¹H NMR spectroscopy. The molecular structures of **3** and **4** have been determined by single-crystal X-ray diffraction. The electronic structure of complex **4** has been examined by DFT.

Introduction

In 2004, Carmona and co-workers reported on the preparation of (C₅Me₅)Zn–Zn(C₅Me₅),¹ the first stable molecular compound containing a Zn–Zn bond. In the following years, further zinc–zinc-bonded complexes such as the ketimate derivative [{HC(CMeNAr)₂}Zn–Zn{HC(CMeNAr)₂}] (Ar = 2,6-*i*-Pr₂C₆H₃),² the dizincocene [(C₅Me₄Et)–Zn–Zn(C₅Me₄Et)],³ and the terphenyldizinc compound Ar'Zn–ZnAr' (Ar' = C₆H₃–2,6-(C₆H₃–2,6-*i*-Pr₂)₂)⁴ have been synthesized. In 2007, we reported on the synthesis and molecular structure of the binuclear zinc complexes (dpp-BIAN)Zn–Zn(dpp-BIAN) (**1**) and of [(dpp-BIAN)Zn(μ-I)]₂ (**2**),⁵ both containing the diimine ligand dpp-BIAN in its radical-anionic form (dpp-BIAN = 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene). The ESR spectra of solutions of **1** confirm the existence of direct Zn–Zn bonds. Compound **1** is easily accessible by reaction of (dpp-BIAN)–

Na₂ with anhydrous ZnCl₂. Complex **2** is obtained by reacting dpp-BIAN with granulated zinc and 0.5 equiv of iodine in THF. In contrast to alkali^{8,9} and alkaline earth metals,¹⁰ metallic zinc does not reduce dpp-BIAN in the absence of iodine.

In the literature concerning zinc–zinc complexes (two reviews have been published just recently^{6,7}) mostly the preparation, structure, and DFT calculations of such compounds are described. So far, data on reactivity of these compounds are scarce. The reactions of (C₅Me₅)Zn–Zn(C₅Me₅) with water or *t*BuOH give C₅Me₅H, Zn(OH)₂, and highly crystalline zinc metal.^{3b} CNXyl reacts with (C₅Me₅)Zn–Zn(C₅Me₅) to give the iminoacyl product (Scheme 1) and metallic zinc.^{3b} The reaction of (C₅Me₅)Zn–Zn(C₅Me₅) with 4-dimethylaminopyridine (dmap) occurs with retention of the Zn–Zn bond and affords the product (Scheme 1) with two molecules of dmap being coordinated to one of the zinc atoms in a geminal fashion.¹¹ Protonation of (C₅Me₅)Zn–Zn(C₅Me₅) with [(2,4,6-Me₃C₆H₂)N(Me)C₂H₃]H (MesnacnacH) gives the dizinc complex (Mesnacnac)Zn–Zn(Mesnacnac) (Scheme 1).¹²

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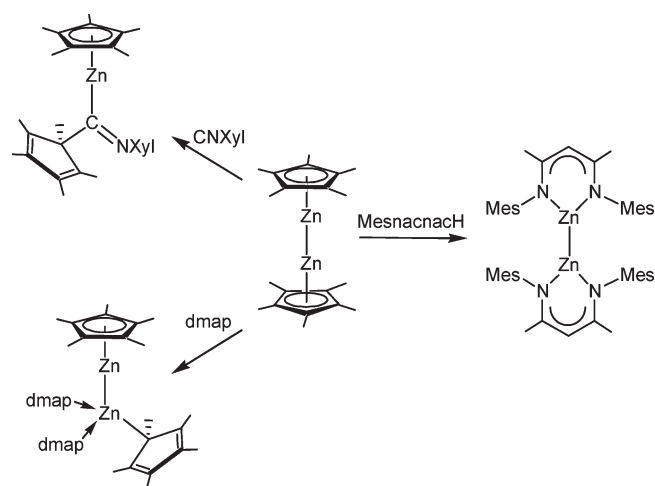
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Scheme 1. Reactivity of $(C_5Me_5)Zn-Zn(C_5Me_5)$ 

Surprisingly, $(Mesnacnac)Zn-Zn(Mesnacnac)$ cannot be prepared by reduction of $(Mesnacnac)ZnX$ ($X = Cl, I$)¹³ with alkali metals, a method that has been successfully applied for the synthesis of the related ketiminate derivative $\{[HC(CMeNAr)_2]Zn-Zn\{HC(CMeNAr)_2\}\}$ ($Ar = 2,6-iPr_2C_6H_3$).²

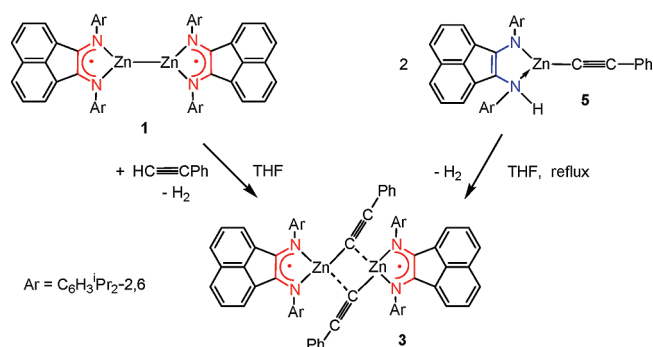
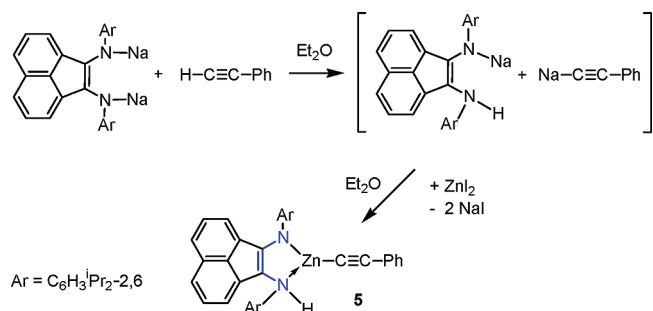
Here we report on the reactions of $(dpp-BIAN)Zn-Zn(dpp-BIAN)$ (**1**) with phenylacetylene and of the iodine-bridged dimer $[(dpp-BIAN)Zn(\mu-I)]_2$ (**2**) with potassium hydride.

Results and Discussion

Since $(dpp-BIAN)Zn-Zn(dpp-BIAN)$ (**1**) contains the dpp-BIAN ligand in the redox-active radical-anionic form,⁸ two main reaction pathways are expected for this compound: (i) reactions causing oxidation or reduction of the dpp-BIAN ligand and (ii) reactions that involve the Zn–Zn bond while maintaining the oxidation state of the dpp-BIAN ligand.

In 2007, Yang et al. reported on the isolation of $Na_2[(dpp-DAD)Zn-Zn(dpp-DAD)]$ ¹⁴ ($dpp-DAD = 1,4$ -bis(2,6-diisopropylphenyl)-1,3-diazadiene), a complex in which the Zn–Zn bond is supported by dianionic diimine ligands. They prepared the complex by reduction of $(dpp-DAD)ZnCl_2$ with 3 equiv of sodium. Stimulated by this result, we reduced **1** with 2 equiv of sodium in diethyl ether in order to obtain the analogous complex $Na_2[(dpp-BIAN)Zn-Zn(dpp-BIAN)]$ with dianionic dpp-BIAN ligands. However, this reaction proceeds with formation of $(dpp-BIAN)Na_2(Et_2O)_3$ and probably metallic zinc.

Due to the ability of dpp-BIAN to act as dianionic ligand $dpp-BIAN^{2-}$, one can expect that in solutions of **1** an equilibrium between $(dpp-BIAN)Zn-Zn(dpp-BIAN)$ and two $(dpp-BIAN)Zn(L)_n$ moieties will exist. The solvated mononuclear zinc complex $(dpp-BIAN)^{2-}Zn^{2+}(L)_n$ is an analogue of the known magnesium complexes $(dpp-BIAN)^{2-}Mg^{2+}(L)_n$ ($L = Et_2O, n = 2; L = THF, n = 3$).^{10,15} Since one of the typical reactions of these magnesium

Scheme 2. Synthesis of Complex **3**Scheme 3. Synthesis of Complex **5**

complexes is the addition of proton acidic substrates to give diamagnetic amido-imino complexes, for instance in the reaction of $(dpp-BIAN)Mg(THF)_3$ with phenylacetylene yielding $[dpp-BIAN(H)]MgC\equiv CPh(L)_n$,¹⁶ we decided to test the reactivity of **1** toward phenylacetylene.

Synthesis of $[(dpp-BIAN)Zn(\mu-C\equiv CPh)]_2$ (3**), $[(dpp-BIAN)Zn(\mu-H)]_2$ (**4**), and $[dpp-BIAN(H)]Zn(C\equiv CPh)$ (**5**).** In contrast to the above reflections, the reaction of $(dpp-BIAN)Zn-Zn(dpp-BIAN)$ (**1**) with phenylacetylene in THF does not produce an amido-imino complex of the type $[dpp-BIAN(H)]Zn(C\equiv CPh)_n$, but proceeds with formation of the binuclear zinc complex **3** and elimination of hydrogen. Compound **3** is also the product of the thermal dehydrogenation of **5** in refluxing THF (Scheme 2). Since **5** is thermally quite stable under these conditions, the dehydrogenation reaction takes several days. However, the reaction can be accelerated by addition of benzophenone, which might act as a trap of hydrogen. Both reactions afford complex **3** as deep red crystals.

Compound **5** itself has been prepared in a two-step one-pot reaction from phenylacetylene, $(dpp-BIAN)Na_2(Et_2O)_3$,⁸ and ZnI_2 in diethyl ether (Scheme 3).

Unfortunately, the isolated air- and moisture-sensitive, deep blue almost black crystals of **5** were not suitable for X-ray structure analysis, but the constitution of **5** was confirmed by its ¹H NMR spectrum. In free dpp-BIAN and all its metal complexes, the steric conditions cause an orthogonal arrangement of the N-bonded phenyl rings with respect to the acenaphthene plane and an arrangement of the isopropyl substituents of the phenyl groups at different sides of the phenyl ring planes. Hence, two times four NMR equivalent methyl groups will give rise for two doublet signals in the ¹H NMR spectrum of such compounds.

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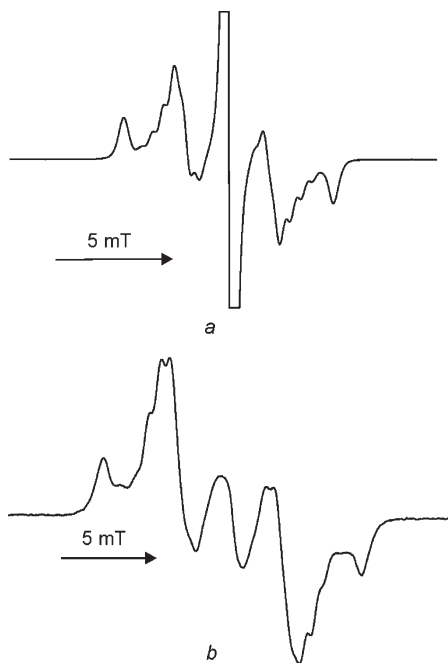
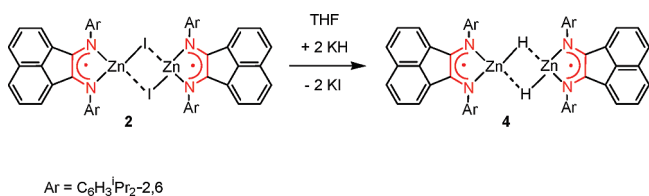


Figure 1. ESR spectra of complexes **3** (a) and **4** (b) (toluene, 150 K).

Scheme 4. Synthesis of Complex 4



This situation will not be maintained if the proton is fixed to one of the two nitrogen atoms. In this case all eight methyl groups are nonequivalent. However, if the proton in dpp-BIAN(H) is localized symmetrically between the two nitrogen atoms and out of the acenaphthene plane, one can expect two methine proton signals and four doublets for the CH₃ groups. The ¹H NMR spectrum of **5**, recorded in THF-*d*₈, shows a singlet for the proton of the dpp-BIAN(H) ligand at $\delta = 6.45$ ppm and four doublet signals for the protons of the eight methyl groups of the isopropyl substituents at $\delta = 1.44$, 1.32, 1.06, and 0.96 ppm. These findings correspond with those obtained for the magnesium complex [dpp-BIAN(H)]-MgC≡CPh(THF)₂¹⁶ and confirm the existence of the proton and its delocalization between the two nitrogen atoms of the dpp-BIAN system. The two pairs of equivalent isopropyl methine protons give rise to two septets at $\delta = 3.96$ and 3.72 ppm. The high-field septet partially overlaps with the signal of the solvent THF-*d*₈.

[(dpp-BIAN)Zn(μ-H)]₂ (**4**) has been prepared by reaction of [(dpp-BIAN)Zn(μ-I)]₂ (**2**) with 2 equiv of potassium hydride in THF and was isolated as deep red crystals by crystallization from toluene (Scheme 4). The IR spectrum of complex **4** reveals the Zn–H stretching vibrations at 1534 cm^{−1}.

The ESR spectra of the paramagnetic compounds **3** and **4** (Figures 1a and 1b), recorded in toluene at 150 K, prove the biradical character of both complexes. In both cases, one electron is localized on each of the two diimine ligands. The additional hyperfine structure was observed for *D*_⊥

Table 1. Crystal and Refinement Data for 3 and 4

	3	4
empirical formula	C ₁₀₀ H ₁₀₂ N ₄ Zn ₂	C ₈₆ H ₉₈ N ₄ Zn ₂
<i>M</i>	1490.60	1318.42
<i>T</i> /K	100(2)	150(2)
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	15.8637(8)	16.2063(3)
<i>b</i> /Å	15.0628(7)	15.1241(3)
<i>c</i> /Å	17.0662(8)	15.2238(3)
α/deg	90	90
β/deg	93.2260(10)	104.4886(18)
γ/deg	90	90
<i>V</i> /Å ³	4071.5(3)	3612.77(12)
<i>Z</i>	2	2
<i>d</i> _{calc} /Mg m ^{−3}	1.216	1.212
μ(Mo Kα)/mm ^{−1}	0.639	0.711
<i>F</i> (000)	1580	1404
cryst size/mm	0.28 × 0.27 × 0.20	0.23 × 0.22 × 0.18
θ range/deg	1.80–25.50	2.92–25.00
<i>h</i> , <i>k</i> , <i>l</i>	−19 ≤ <i>h</i> ≤ 19 −18 ≤ <i>k</i> ≤ 18 −20 ≤ <i>l</i> ≤ 20	−19 ≤ <i>h</i> ≤ 19 −17 ≤ <i>k</i> ≤ 17 −18 ≤ <i>l</i> ≤ 17
reflns collected	33 048	33 012
indep reflns	7546	6356
<i>R</i> (int)	0.0288	0.0621
data/restraints/params	7546/9/689	6356/0/418
GOF	1.059	1.003
<i>R</i> ₁ / <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0311/0.0772	0.0461/0.1005
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0396/0.0805	0.0795/0.1118
largest diff peak, hole/e Å ^{−3}	0.497/−0.178	0.522/−0.368

components due to the splitting on the four equivalent N nuclei (*I* = 1, simulated *A*_⊥(N) = 6.5 G). The spectra also show half-field signals ($\Delta m_s = 2$), which are typical for biradicals. On the basis of the spectral parameters the distance between the unpaired electrons in **3** and **4** has been calculated to be 7.67 Å (*D* = 61.0 G) and 7.76 Å (*D* = 59.5 G), respectively. These data agree well with the results of the X-ray structure analyses.

Molecular Structures of Compounds 3 and 4. The crystal and structure refinement data of **3** and **4** are listed in Table 1, and their molecular structures are depicted in Figures 2 and 3. The molecules of **3** and **4** are centrosymmetric dimers with an inversion center localized in the middle between the two zinc atoms. In both molecules the zinc atoms are coordinated tetrahedrally. Just as the ESR data, the molecular parameters of **3** and **4** confirm the radical-anionic character of the dpp-BIAN ligands. While in free dpp-BIAN¹⁷ the distances N(1)–C(1) and N(2)–C(2) (both 1.282(4) Å) correspond to a carbon–nitrogen double bond and the C(1)–C(2) distance (1.534(6) Å) is typical for a single carbon–carbon bond, in **3** and **4** the N(1)–C(1) and N(2)–C(2) bonds are elongated and the respective C(1)–C(2) distance is shortened compared to free dpp-BIAN (**3**: C(1)–N(1) 1.3365(15), C(2)–N(2) 1.3291(15), C(1)–C(2) 1.4408(16) Å; **4**: C(1)–N(1) 1.319(4), C(2)–N(2) 1.338(4), C(1)–C(2) 1.437(4) Å). According to the symmetry of the LUMO of dpp-BIAN, these structural changes correspond with the population of this orbital by an electron.

In **3** as well as in **4** the planes of the two acenaphthenediiimine units run parallel to each other and orthogonal to the plane of the respective four-membered metalacycle formed by the atoms Zn(1) and Zn(1a) and the bridging carbon atoms (**3**) or bridging hydrogen atoms (**4**). In **3** the distances of the zinc atoms to the bridging carbon atoms are

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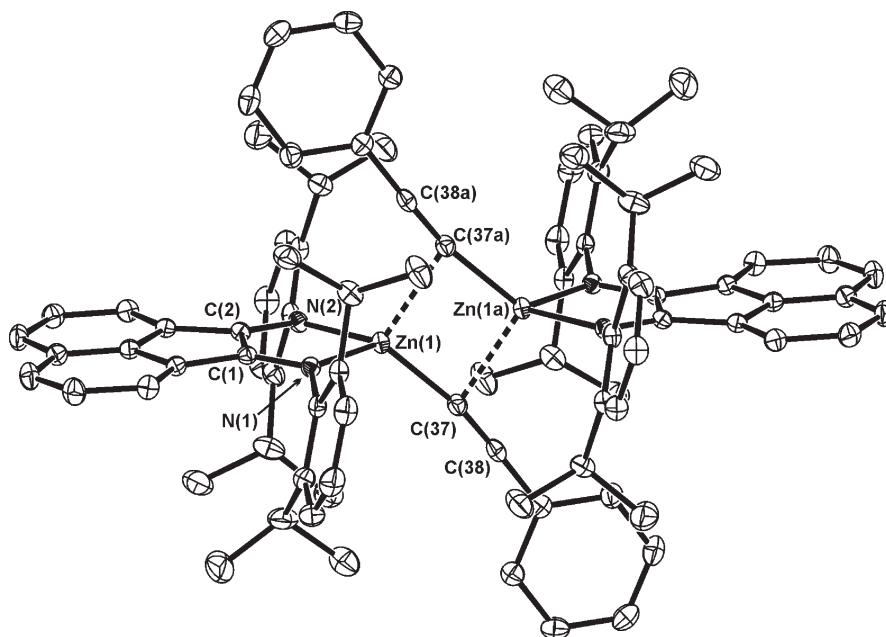


Figure 2. Molecular structure of **3**. Thermal ellipsoids are drawn at 40% probability. The hydrogen atoms are omitted. Selected bond lengths (Å) and angles (deg): Zn(1)–N(1) 2.0063(10), Zn(1)–N(2) 1.9996(10), Zn(1)–C(37) 1.9840(12), Zn(1)–C(37a) 2.2569(12), Zn(1)···Zn(2) 2.7816(3), C(1)–N(1) 1.3365(15), C(2)–N(2) 1.3291(15), C(1)–C(2) 1.4408(16), C(37)–C(38) 1.2099(17); N(1)–Zn(1)–N(2) 86.56(4), C(37)–Zn(1)–C(37a) 98.30(4), N(1)–Zn(1)–C(37) 125.09(4), N(1)–Zn(1)–C(37a) 114.93(4), N(2)–Zn(1)–C(37) 120.73(4), Zn(1)–C(37)–Zn(1a) 81.70(4), Zn(1)–C(37)–C(38) 170.08(11), Zn(1)–C(37a)–C(38a) 108.22(9).

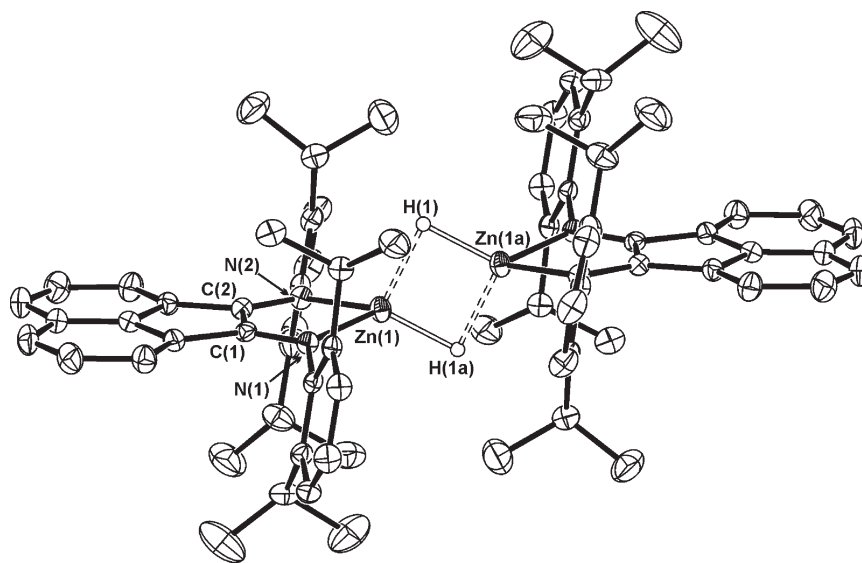


Figure 3. Molecular structure of **4**. Thermal ellipsoids are drawn at 40% probability. The hydrogen atoms except H(1) and H(1a) are omitted. Selected bond lengths (Å) and angles (deg): Zn(1)–N(1) 1.994(2), Zn(1)–N(2) 2.012(2), Zn(1)–H(1a) 1.67(3), Zn(1)–H(1) 1.88(3), Zn(1)···Zn(2) 2.4785(6), C(1)–N(1) 1.319(4), C(2)–N(2) 1.338(4), C(1)–C(2) 1.437(4); N(1)–Zn(1)–N(2) 85.67(9), H(1)–Zn(1)–H(1a) 91.7(13), N(1)–Zn(1)–H(1) 115.1(8), N(1)–Zn(1)–H(1a) 121.0(10), N(2)–Zn(1)–H(1a) 132.3(9).

quite different (Zn(1)–C(37) 1.9840(12), Zn(1)–C(37a) 2.2569(12) Å). The long Zn(1)–C(37a) bond as well as the elongation of the C(37a)–C(38a) bond (1.2099(17) Å) compared to the length of the C≡C bond in free phenylacetylene (1.188(2) Å)¹⁸ may be explained by π -electron donation from the ethynyl bond into vacant zinc orbitals. The angles Zn–C(37)–C(38) (170.08(11)°) and Zn(1)–C(37a)–C(38a)

(108.22(9)°) correspond with a nearly linear and a nearly right-angled Zn–C≡CPh arrangement. The comparison of the bonding situation in **3** with that in [(TMEDA)Na(C≡CPh)₂Zn(*t*Bu)]₂,¹⁹ also a complex in which the zinc atoms are bridged by C≡CPh ligands (Zn–C(≡C) 2.118(5) and 2.292(5) Å; Zn–C≡C 158.0(5)° and 121.4(4)°), shows

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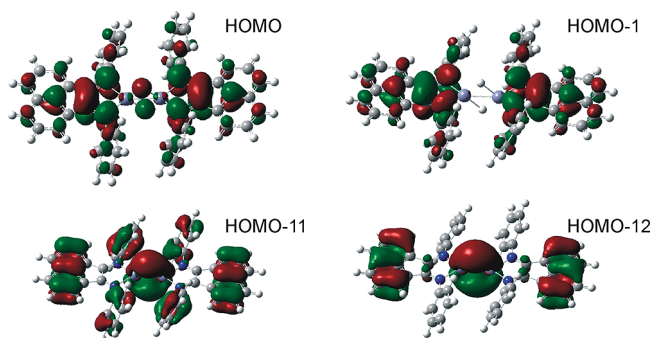


Figure 4. HOMO, HOMO–1, and HOMO–11 α orbitals of **4** from DFT calculation.

that the coordination of the ethynyl ligands is less symmetric in **3** than in $[(\text{TMEDA})\text{Na}(\text{C}\equiv\text{CPh})_2\text{Zn}(\text{tBu})_2]$. In $[(\text{TMEDA})\text{Li}(\text{C}\equiv\text{CPh})_2\text{Zn}(\text{tBu})_2(\text{TMEDA})]$,¹⁹ in which two phenylethynyl groups bridge a zinc and a lithium atom, the two $\text{Zn}-\text{C}(\equiv\text{CPh})$ bonds show nearly the same length (2.0495(18) and 2.0738(18) Å), whereas the bond angles $\text{Zn}-\text{C}\equiv\text{C}(\text{Ph})$ correspond with those in **3** ($\text{Zn}-\text{C}\equiv\text{C}$ 173.64(15)° and 105.37(16)°).

Like the molecules of **3**, the molecules of **4** show different distances between the zinc atoms and the bridging ligands ($\text{Zn}(1)-\text{H}(1)$ 1.88(3) and $\text{Zn}(1)-\text{H}(1a)$ 1.67(3) Å). In the other two hydrogen-bridged binuclear zinc complexes known so far, $\text{Ar}'\text{Zn}(\mu-\text{H})_2\text{ZnAr}'$ ($\text{Ar}' = \text{C}_6\text{H}_3-2,6\text{-}(\text{C}_6\text{H}_3-2,6\text{-}i\text{Pr}_2)_2$);⁴ $\text{Zn}-\text{H}$ (1.67(2) and 1.79(3) Å) and $[\text{HC}(\text{CMe-NAr})_2]\text{Zn}(\mu-\text{H})_2$ ($\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$);²⁰ $\text{Zn}-\text{H}$ (1.766 Å), the difference in the length of the $\text{Zn}-\text{H}$ bonds is considerably smaller or even zero. The $\text{Zn}-\text{H}$ bonds in **4** are also remarkably longer than the terminal $\text{Zn}-\text{H}$ bonds in $[\text{Me}_2\text{N}(\text{CH}_2)_2\text{N}(\text{Me})\text{ZnH}]_2$ (1.62 Å)²¹ or $[(\text{Me}_3\text{PN})\text{ZnH}]_4$ (1.50 Å).²² Due to the small ionic radius of the hydride ion, the $\text{Zn}\cdots\text{Zn}$ separation in **4** (2.4785(6) Å) is smaller than in **3** (2.7816(3) Å). However, both distances exceed the range of direct zinc–zinc bonds (2.29–2.40 Å).⁶

The electronic structure of **4** was examined by DFT²³ calculations at the B3LYP/6-31G* level using the molecule with unsubstituted phenyl fragments as a model system. Recently, we used such calculations to study the $\text{Zn}-\text{Zn}$ bonding in **1**.⁵ The triplet ground-state configuration of **4** is 11.0 kcal mol^{−1} more stable than the lowest singlet state, which agrees well with the ESR data obtained for **4**. The key MOs of **4** are depicted in Figure 4. Like in **1**, the two highest semi-occupied MOs of the triplet system of **4** are localized on the dpp-BIAN ligands, but in contrast to **1** (HOMO and HOMO–1; −3.95 eV), in **4** these MOs are not degenerate (HOMO, −3.89 and HOMO–1, −4.08 eV). The α HOMO and HOMO–1 in **4** are mainly localized on the atoms of the diimine fragments and partially on the bridging hydrogen atoms. The degenerate α HOMO–11 and HOMO–12 (−6.75 eV) are responsible for the $\text{Zn}-\text{H}-\text{Zn}$ bonding.

According to the natural bond orbital (NBO) analysis, the covalent contribution to the $\text{Zn}-\text{H}$ bonding arises from the

donation of the s lone pair of the hydrogen anion to the vacant Zn level (97.6% s, 1.8% p, 0.2% d). The natural charge of Zn is 1.44 e, thus being 0.60 e more positive than in **1**.⁵ Each bridging hydrogen atom bears a natural charge of −0.63 e, compensating the decrease in the metal electron density and providing a more ionic character of the bonding between the (dpp-BIAN) ZnH monomers in **4** than between the (dpp-BIAN) Zn monomers in **1**.

Experimental Section

General Remarks. Compounds **3**, **4**, and **5** are sensitive to air and moisture. Therefore all manipulations concerning their preparation and identification were carried out under vacuum using Schlenk techniques. The solvents THF, diethyl ether, benzene, and toluene were dried by distillation from sodium/benzophenone. THF-*d*₈ (Aldrich) used for the NMR measurements was dried with sodium/benzophenone at ambient temperature just prior to use and was condensed under vacuum into the NMR tube already containing the sample. The IR spectra were recorded on a FSM-1201 spectrometer; the ¹H NMR spectra, on a Bruker DPX-200 NMR spectrometer. The ESR spectra were obtained using a Bruker EMX instrument equipped with an ER 041X microwave bridge.

Synthesis of [(dpp-BIAN)Zn(μ -C≡CPh)]₂ (3**). Method A.** To a solution of **1** (0.54 g, 0.48 mmol) in THF (30 mL) was added phenylacetylene (0.10 g, 0.960 mmol). During 48 h of reflux the color of the reaction mixture changed from gold-red to cherry-red. The solid that remained after evaporation of the solvent under vacuum was crystallized from benzene, giving red crystals of **3**. Yield: 0.19 g (27%). Mp > 257 °C (dec). Anal. Found (%): C 80.31, H 7.20. Calcd for C₁₀₀H₁₀₂N₄Zn₂ (1490.60 g/mol) (%): C 80.58, H 6.90. IR (Nujol): 3058 w, 3031 w, 2089 m, 1808 w, 1596 w, 1534 s, 1361 m, 1319 s, 1254 m, 1184 m, 1157 w, 1146 w, 1107 w, 1080 w, 1057 w, 1038 w, 1011 w, 961 w, 946 w, 934 w, 865 m, 819 m, 803 m, 784 m, 761 s, 592 w, 534 m, 453 m, 411 s cm^{−1}. **Method B.** To a solution of compound **5** (0.67 g, 1 mmol) in THF (40 mL) was added benzophenone (0.09 g, 0.5 mmol). In the course of 20 h reflux, the mixture changed color from deep blue to cherry-red. Then the solvent was evaporated under vacuum. Crystallization of the residual solid from benzene gave red crystals of **3**. Yield: 0.25 g (34%).

Synthesis of [(dpp-BIAN)Zn(μ -H)]₂ (4**).** To a solution of **2** (prepared from 0.5 g (1 mmol) of dpp-BIAN, 0.13 g (0.5 mmol) of iodine, and an excess of the granulated zinc in THF (30 mL)) was added potassium hydride (0.04 g, 1 mmol). In the course of 18 h stirring of the mixture at room temperature its color changed from cherry-red to red-brown. After evaporation of the solvent under vacuum the residue was dissolved in toluene (30 mL) and filtered off from precipitated KI. Reduction in the volume of the solution and cooling caused precipitation of 0.44 g (67%) of **4** as red-brown crystals. Mp > 263 °C (dec). Anal. Found (%): C 78.08, H 7.81. Calcd for C₈₆H₉₈N₄Zn₂ (1318.42 g/mol): C 78.35, H 7.49. IR (Nujol): 1534 s, 1318 m, 1257 m, 1184 m, 1154 w, 1103 w, 1080 m, 1057 m, 1034 w, 934 m, 864 w, 819 m, 799 c, 757 s, 692 m, 668 w, 634 m, 542 m cm^{−1}.

[(dpp-BIAN(H))Zn(C≡CPh)] (5**).** To a solution of Na₂(dpp-BIAN) (freshly prepared from 0.046 g (1 mmol) of Na and 0.5 g (1 mmol) of dpp-BIAN in Et₂O (30 mL)) was added phenylacetylene (0.102 g, 1 mmol). The color of the reaction mixture changed instantly from deep green to deep blue. To this mixture was added a solution of ZnI₂ (prepared prior to use from excess zinc metal and iodine (0.254 g, 1 mmol) in Et₂O (20 mL)), and the NaI formed was filtered off. In the course of 1 day, **5** (0.73 g, 86%) separates from the mother liquor as deep blue crystals. Mp > 275 °C (dec). Anal. Found (%): C 75.92, H 7.88. Calcd for C₅₄H₇₁N₃ZnO₂ (845.55 g/mol): C 76.71, H 8.46. IR (Nujol): 3258 w, 3054 w, 2096 m, 1931 w, 1804 w, 1673 w, 1589 m, 1519 s, 1362 m, 1319 m, 1258 s, 1185 m, 1108 m, 1058 m, 1039 w, 1008 w,

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(23) The geometry optimization, single-point calculation, and NBO analysis were performed using the Gaussian 03 package (see Supporting Information).

935 w, 916 s, 870 w, 850 w, 820 m, 800 m, 785 w, 758 s, 693 s, 665 w, 627 w, 596 w, 546 s, 535 s, 493 w, 454 m, 408 s cm^{-1} . ^1H NMR ($\text{THF}-d_8$): δ 7.35 (d, 1 H, Ar, $J=7.8$ Hz), 7.29–7.10 (m, 4 H, Ar), 6.97–6.88 (m, 2 H, Ar), 6.85–6.73 (m, 3 H, Ar), 6.45 (s, 1 H, NH), 6.12 (d, 1 H, Ar $J=7.0$ Hz), 5.81 (d, 1 H, Ar, $J=6.0$ Hz), 3.96 (br sept, 2 H, CH), 3.72 (br sept, 2 H, CH), 1.44 (d, 6 H, $\text{CH}_3(i\text{Pr})$, $J=6.5$ Hz), 1.32 (d, 6 H, $\text{CH}_3(i\text{Pr})$, $J=6.5$ Hz), 1.06 (br s, 6 H, $\text{CH}_3(i\text{Pr})$), 0.96 (d, 6 H, $\text{CH}_3(i\text{Pr})$, $J=6.8$ Hz).

X-ray Crystal Structure Determination of Compounds 3 and 4.

The crystal data of **3** were collected at 100 K on a Bruker SMART APEX diffractometer; those of **4**, at 150 K on an Oxford Diffraction Xcalibur S Sapphire diffractometer using graphite-monochromated Mo K α ($\lambda=0.71073$ Å) radiation.

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(26) Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.

SADABS²⁴ was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods using SHELXS-97²⁵ and refined by full-matrix least-squares techniques against F_o^2 using SHELXL-97.²⁶ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å².

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Supporting Information Available: Full details of the X-ray structural analyses of compounds **3** and **4** and full reference for the Gaussian 03 program are available free of charge via the Internet at <http://pubs.acs.org>.