Synthesis, Structure and Reactivity of a Tetranuclear Amidinato Zinc Hydride Complex

Benjamin Gutschank, Stephan Schulz, Dieter Bläser, Roland Boese and Christoph Wölper*

Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany

E-mail: stephan.schulz@uni-due.de

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

* To whom correspondence should be addressed. Prof. Dr. Stephan Schulz, Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany; Phone: +49 0201-1834635; Fax: +49 0201-1834635; homepage: http://www.uni-due.de/ak_schulz/index.php

Summary: The tetranuclear amidinato zinc hydride complex $\{C[C(Ni-Pr)_2ZnH]_4\}$ **3** was synthesized by reaction of the Cl-substituted complex $\{C[C(Ni-Pr)_2ZnCl]_4\}$ with CaH_2 . **3** was found to react with phenylacetylene and acetylene at ambient temperature with elimination of H_2 and subsequent formation of $C[C(Ni-Pr)_2ZnC\equiv CPh]_4$ **4** and $\{C[C(Ni-Pr)_2ZnC\equiv CH]_4\}$ **5**, respectively. **3** – **5** have been characterized by multinuclear NMR (1H , ^{13}C) and IR spectroscopy, elemental analyses and by single-crystal X-ray diffraction.

KEYWORDS. Hydrides, Acetylides, Zinc, X-Ray Diffraction.

Introduction. The reactions of main group and transition metal alkyl complexes with carbodiimides $C(NR)_2$ typically proceed with insertion of the carbodiimide into a metal-carbon bond and subsequent formation of the corresponding amidinate complexes.^[1] In remarkable contrast, we found that dimethylzinc reacts with $C(NR)_2$ ($R = i\text{-Pr}$; Cy) at elevated temperatures with elimination of methane and unforeseen formation of tetranuclear amidinate complexes such as $\{C[C(NR)_2ZnMe]_4\}$ ($R = i\text{-Pr}$ **1a**; Cy **1b**).^[2] Due to the presence of four Zn-Me moieties, these complexes were expected to be suitable starting reagents for further substitution reactions. However, reactions of **1a** with H-acidic amines RNH_2 , alcohols ROH and even water at ambient temperature did not occur, whereas at elevated temperatures the complexes completely decomposed due to protonation of the Lewis basic N centers rather than to give the expected methane elimination products. We therefore synthesized the corresponding halide-substituted complexes $\{C[C(Ni\text{-}Pr)_2ZnX]_4\}$ ($X = Cl$ **2a**, Br **2b**, I **2c**) by a methyl/halide exchange reaction with AlX_3 in order to investigate substitution reactions at the Zn centers via salt elimination pathways.^[3] However, a major drawback of salt elimination reactions using Li organyls and Grignard reagents is the formation of solid byproducts, necessitating further purification steps. We therefore became interested in the tetranuclear zinc hydride complex $\{C[C(Ni\text{-}Pr)_2ZnH]_4$ since the Zn-H groups were expected to show an increased reactivity towards hydrogen elimination, insertion reactions or addition reactions.

Herein we report on the synthesis and crystal structure of $\{C[C(Ni\text{-}Pr)_2ZnH]_4$ **3**. Moreover, initial studies on its reactivity towards C-H acidic organic substrates such as acetylene $HC\equiv CH$ and phenylacetylene $HC\equiv CPh$ proved **3** to be a suitable starting reagent for substitution reactions (hydrogen elimination) under mild reaction conditions. These reactions were found to proceed with preservation of the central cluster-like zinc amidinate core and subsequent formation of $\{C[C(Ni\text{-}Pr)_2ZnC\equiv CPh]_4$ **4** and $\{C[C(Ni\text{-}Pr)_2ZnC\equiv CH]_4$ **5**, respectively. **5** represents the first structurally characterized Zn complexes containing covalently-bound, terminal $C\equiv CH$ groups.

Results and Discussion. The reaction of $\{C[C(Ni-Pr)_2ZnCl]_4\}$ **2a** with an excess of CaH_2 in THF at 0 °C gave **3** in high yield after workup.

((Scheme 1 here))

The 1H NMR spectrum of the bulk reaction mixture shows the typical resonance pattern due to two nonequivalent *i*-Pr groups as was observed for the halide substituted complexes $\{C[C(Ni-Pr)_2ZnX]_4\}$.^[3] An additional sharp singlet (4.60 C_6D_6 ; 4.11 THF- D_8), which is in the typical range previously observed for Zn-H groups,^[4] prove the formation of the zinc-hydride moiety. The IR spectrum of **3** shows a strong Zn-H valence vibration band at 1766 cm^{-1} , in accordance with values previously reported for zinc complexes containing terminal hydrides such as $[HZnOtBu]_4$ (1821 cm^{-1})^[5] and $[tris(3\text{-tert-butylpyrazolyl})hydroborat]ZnH$ (1770 cm^{-1}).^[6]

((Figure 1 here))

Colorless crystals of **3** suitable for single crystal X-ray diffraction determination were obtained from a solution in THF at -30 °C. **3** crystallizes in the monoclinic space group $C2/c$. The cluster-like core as was observed in the starting complex **2a** is still preserved. The central sp^3 -hybridized C_{center} atom is coordinated by four C atoms of adjacent amidinate groups and the C-C bond lengths are in the range of typical C-C single bonds ($1.559(0)$ - $1.560(7)\text{ Å}$). The N-C bond lengths within the amidinate groups indicate an almost perfectly delocalized π -electron system (average value 1.330 Å). Almost analogous structural parameters were observed in **1a** and **2a-c**, respectively. The Zn atoms in **3**, which bind to three N atoms of adjacent amidinate groups and an additional H atom, adopt tetrahedral coordination spheres. The Zn-N bond lengths in **3** ($2.1266(16)$ - $2.1445(17)\text{ Å}$) are almost identical to those of **1a** and **2a-c** and the Zn-H bond length ($1.46(3)\text{ Å}$) is within the range previously reported for terminal zinc hydrides.^[6,7] Zinc hydrides containing terminal Zn-H groups are still rare and **3** is only the second example of a complex containing four terminal Zn-H groups in a single molecule.

((Scheme 2 here))

In order to evaluate the reactivity of the amidinato zinc hydride complex in more detail, **3** was reacted with $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{Ph}, \text{H}$) under mild reaction conditions (ambient temperature, acetylene at atmospheric pressure). These reactions almost quantitatively yielded the corresponding hydrogen elimination products $\{\text{C}[\text{C}(\text{Ni-Pr})_2\text{ZnC}\equiv\text{CPh}]_4$ **4** and $\{\text{C}[\text{C}(\text{NR})_2\text{ZnC}\equiv\text{CH}]_4$ **5** within 24 h.^[8] In contrast, **1a** completely failed to react with phenyl acetylene even at elevated temperatures (110 °C) and long reaction periods (7 d). These findings clearly demonstrate the enhanced reactivity of the Zn-H group compared to the Zn-Me group in complex **1a**, which most likely results from the replacement of the Me group by the sterically less demanding hydride group (kinetically-controlled reaction).

((Figure 2 here))

¹H NMR monitoring of the reaction of **3** and $\text{HC}\equiv\text{CH}$ showed a constantly decreasing Zn-H and an increasing acetylide resonance. The intermediate appearances of four different acetylide resonances of different intensity around 2.1 – 2.15 ppm after 7.5 h (see insert box in Fig. 2) indicate a stepwise substitution of the four hydride centers. The characteristic nonequivalent *i*-Pr resonances of the tetraamidinato framework shifted to lower field with ongoing formation of the complex **5**.

((Figures 3 and 4 here))

Colorless crystals of **4** and **5** suitable for a single crystal structure determination were obtained from solutions in THF. **4** crystallizes in the orthorhombic space group *Pbcn* containing three disordered THF molecules in the unit cell, whereas **5** crystallizes in the triclinic space group *P*-1. Both complexes again show the cluster-like core with the central sp^3 -hybridized C_{center} atom. The C-C (**4**: 1.557(7) - 1.564(9), **5**: 1.555(1) - 1.567(0) Å) and N-C bond lengths (average values: **4** 1.332 Å, **5** 1.330 Å) within this core are almost unchanged compared to **3** and again indicate delocalized π -electron systems within the amidinate groups. The Zn atoms in **4** and **5** are tetrahedrally coordinated by three N atoms of adjacent amidinate groups and the acetylide moiety. The Zn-N (**4**: (2.0986(10)-2.1768(11); **5** (2.092(8)-2.137(8) Å) and Zn-C bond lengths (**4**: 1.926(1)-1.930(8); **5**: 1.925(6)-1.948(7) Å) are very similar. The C-C

bond lengths of the ethynyl groups in **4** (1.208(4)-1.210(3) Å) are slightly elongated compared to that in free phenylacetylene (1.183 Å),^[9] but comparable to values reported for [Zn(C≡CSiMe₃)(NPM₃)₄] (1.20(2) Å), [Zn(C≡C-C≡CSiMe₃)(NPEt₃)₄] (1.22(1) Å),^[10] [(dpp-BIAN)Zn(μ-C≡CPh)]₂ (1.2099(17) Å),^[11] DippNacNacZnC≡CPh (1.207(3) Å),^[12] as well as to the base-stabilized complex (PhC≡C)₂Zn(tmeda) (1.211(5), 1.219(5) Å),^[13] respectively. The C≡C triple bond lengths in **5** (1.170(5)-1.183(3) Å) are shorter than in **4** but comparable to that reported for free acetylene (1.126(8) Å at 140K).^[14] The M-C-C angles in **5** are almost linear with values around 177.5° whereas the angles in **4** show a rather unusual trend. The Zn2-C12-C13 unit (178.8°) shows an almost perfect linear arrangement, whereas the Zn1-C4-C5 bond angle (164.4°) significantly differs from linearity. *Green et al.* reported on similar structural findings for group 2 metal acetylides of the type [M([18]crown-6)(C≡CSiPh₃)₂] (M = Ca, Sr) and explained the bending by packing effects due to space limitations and a low energy barrier for the bending.^[15] Moreover, *Clegg et al.* recently reported that C≡C-Zn bond angles typically lie in the range of 164.2-175.5°.^[13]

Zinc acetylide complexes of the general type LZnC≡CH have only been scarcely described in the literature. To the best of our knowledge, the ionic zincates K₂Zn(C≡CH)₄·2NH₃ and Rb₂Zn(C≡CH)₄^[16] are the only structurally characterized complexes of this type. **5** therefore represents the first structurally characterized neutral Zn acetylide complex containing a covalently bound, terminal C≡CH moiety.

Conclusions. {C[C(NR)₂ZnH]₄ **3** is a valuable starting reagent for further substitution reactions due to its enhanced reactivity toward organic substrates containing acidic H-atoms. Reactions with acetylenes were found to occur under very mild reaction condition with stepwise elimination of hydrogen and subsequent formation of {C[C(Ni-Pr)₂ZnC≡CPh]₄ **4** and {C[C(Ni-Pr)₂ZnC≡CH]₄ **5**, the first structurally characterized neutral zinc acetylide complex.

Experimental Details. All manipulations were performed in a glovebox under an Ar atmosphere or using standard Schlenk line techniques. Solvents were carefully dried over Na/K and degassed prior to

use. **2a**^[3] and sodium phenylacetylene^[17] were prepared according to literature methods. ¹H and ¹³C NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal C₆D₅H (¹H: δ = 7.154; ¹³C: δ = 128.0), THF-D₈ (¹H: δ = 3.58, 1.73) or CDCl₃ (¹H: δ = 7.26; ¹³C: δ = 77.0). IR spectra were recorded on an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Essen.

{C[C(Ni-Pr)₂ZnH]₄} 3. 0.4 g (0.4 mmol) of **2a** and 0.04 g (0.9 mmol) of CaH₂ were suspended in 15 mL of THF, stirred for 3 d at 0 °C and then filtered. The filtrate was stored at -30 °C, yielding colorless crystals of **3** after 24 h.

Yield: 0.31 g (91 %). Melting point: 228 °C (dec.). Anal. Found (calcd) for C₂₉H₆₀N₈Zn₄ (782.48 g/mol): H, 7.06 (7.13); C, 44.44 (44.51); N, 14.21 (14.32). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 1.24 (d, 24 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 1.48 (d, 24 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 3.74 (sept, 4 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 4.14 (sept, 4 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 4.67 (s, 4 H, ZnH). ¹H NMR (300 MHz, THF-D₈, 25 °C): δ = 1.22 (d, 24 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 1.41 (d, 24 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 3.90 (sept, 4 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂), 4.67 (s, 4 H, ZnH), 4.32 (sept, 4 H, ³J_{HH} = 6.4 Hz, CH(CH₃)₂). ¹³C NMR (200 MHz, C₆D₆, 25 °C): δ = 24.9 (CH₃), 25.6 (CH₃), 47.6 (CH), 48.9 (CH), 74.3 (C), 169.7 (NCN). ATR-IR: ν = 2958, 2927, 2904, 2864, 1766 (Zn-H), 1560, 1520, 1449, 1386, 1362, 1255, 1079, 1013, 868, 791, 690, 660, 556, 495 cm⁻¹.

{C[C(Ni-Pr)₂ZnCCPh]₄} 4. Method A) A solution of 0.25 g (0.27 mmol) of **2a** in 10 mL of THF were added to a suspension of 0.14 g (1.1 mmol) of NaCCPh in 15 mL of THF. The suspension was stirred for 2 h at 25 °C, filtrated and the filtrate was stored at -30 °C. Colorless crystals of **4** were formed within 24 h. Yield: 0.22 g (68 %). **Method B)** A solution of 0.4 g (1 mmol) **3** and 0.5 mL (1 mmol) phenylacetylene in 20 mL of THF was stirred for 3 h at 60 °C, yielding a yellowish solution that was stored at -30 °C. Colorless crystals of **4** were formed within 24 h. Yield: 0.49 g (81 %).

Melting point: 269 °C (dec.). Anal. Found (calcd) for C₆₁H₇₆N₈Zn₄ (1182.95 g/mol): H, 6.41 (6.48);

C, 61.64 (61.85); N, 8.50 (8.47). ^1H NMR (300 MHz, CDCl_3 , 25 °C): δ = 1.42 (d, 24 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.68 (d, 24 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.03 (sept, 4 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.43 (sept, 4 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.24 (m, 8 H, *m*-H), 7.27 (m, 4 H, *p*-H), 7.43 (m, 8 H, *o*-H). ^{13}C NMR (200 MHz, CDCl_3 , 25 °C): δ = 24.4 (CH_3), 24.8 (CH_3), 48.2 (CH), 49.8 (CH), 72.9 (C), 109.1 (ZnCC), 111.8 (ZnCC), 126.4 (*ipso*-C), 126.8 (*p*-C), 128.2 (*m*-C), 131.5 (*p*-C), 169.5 (NCN). ATR-IR: ν = 2956, 2922, 2895, 2868, 1554, 1516, 1481, 1392, 1363, 1248, 1206, 1121, 1064, 1026, 938, 896, 865, 830, 788, 761, 727, 693, 666, 651, 555, 532, 463, 444 cm^{-1} .

{C[C(Ni-Pr)₂ZnCCH]₄} **5**. 0.4 g (0.5 mmol) of **3** were dissolved in 15 mL of THF and stirred for 1 d at 35 °C under an acetylene atmosphere of 4 bar in a sealed pyrex tube. Colorless crystals of **5** were formed within 24 h after storage at -30 °C.

Yield: 0.38 g (84 %). Melting point: 250 °C (dec.). Anal. Found (calcd) for $\text{C}_{37}\text{H}_{60}\text{N}_8\text{Zn}_4$ (878.57 g/mol): H, 6.81 (6.88); C, 50.63 (50.58); N, 12.61 (12.75). ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ = 1.06 (d, 24 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.40 (d, 24 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.98 (s, 4 H, CCH), 3.47 (sept, 4 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.85 (sept, 4 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$). ^1H NMR (300 MHz, THF- D_8 , 25 °C): δ = 1.36 (d, 24 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.60 (d, 24 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.15 (s, 4 H, CCH), 3.98 (sept, 4 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.41 (sept, 4 H, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (200 MHz, C_6D_6 , 25 °C): δ = 24.2 (CH_3), 24.8 (CH_3), 48.2 (CH), 50.0 (CH), 63.8 (C), 96.7 (ZnCCH), 106.5 (ZnCCH), 169.9 (NCN). ATR-IR: ν = 3278 (sym ZnCC-H), 3259 (asym ZnCC-H), 2959, 2922, 2867, 1564, 1519, 1456, 1386, 1364, 1327, 1304, 1256, 1164, 1123, 1093, 1012, 938, 894, 868, 798, 657, 646, 631, 542, 524 472, 431 cm^{-1} .

Single-crystal X-ray analyses. The crystals were mounted in inert oil on nylon loops. The data were collected on a Bruker D8 Kappa diffractometer with APEX2- detector using monochromated $\text{MoK}\alpha$ -radiation. Crystallographic data for **3**, **4** and **5** are summarized in Table 1. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). The structures were solved by Direct Methods (Bruker AXS APEX2) and refined anisotropically against

F^2 (G. M. Sheldrick SHELXL-97^[18]). Hydrogen atoms were refined using a riding model or ridged methyl groups. In **3** H(1) and H(2) were found in a difference fourier synthesis and refined freely. The high anisotropic displacement parameter of C(51) in **4** indicate a slight disorder, which is too weak to be refined as two alternative positions. In **5** H(31), H(33), H(35) and H(37) were found and refined freely with fixed U. The crystallographic data of the structures (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-790554 (**3**), CCDC-790555 (**4**) and CCDC-790556 (**5**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code_(1223)336-033; E-Mail for inquiry: fileserv@ccdc.cam.ac.uk; E-Mail for deposition: deposit@ccdc.cam.ac.uk).

Acknowledgment. S. Schulz thanks the German Science Foundation (DFG) for financial support.

Supporting Information Available. A CIF file giving X-ray crystallographic data of **3**, **4**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

FIGURE CAPTIONS

Figure 1. Molecular structure of $\{C[C(Ni-Pr)_2ZnH]_4$ **3** (thermal ellipsoids are shown at 50% probability levels). H atoms except for Zn-H ones are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Zn1-H1 1.45(3), Zn2-H2 1.47(3), Zn1-N1 2.1273(17), Zn1-N2 2.1428(16), Zn1-N4 2.1357(16), Zn2-N2 2.1445(17), Zn2-N3 2.1266(16), Zn2-N4 2.1372(17), N1-C14 1.314(2), N2-C14a 1.344(2), C13-C14 1.559(2), C13-C15 1.561(2); N1-C14-N2a 137.27(18), N3a-C15-N4 137.44(18), C14-C13-C15 100.42(10), C14a-C13-C15 130.06(10), N1-Zn1-N2 96.19(6), N1-Zn1-N4 97.25(6), N2-Zn1-N4 83.00(6), N2-Zn2-N3 96.80(6), N2-Zn2-N4 82.92(6), N3-Zn2-N4 97.01(6).

Figure 2. Time-dependent ^1H NMR monitoring of the reaction of **3** and $\text{HC}\equiv\text{CH}$ in THF-D_8 (Zn-H indicated by *, Zn-C $\equiv$ CH by #).

Figure 3. Molecular structure of $\{C[C(Ni-Pr)_2ZnC\equiv\text{CPh}]_4$ **4** (thermal ellipsoids are shown at 50% probability levels). H atoms are omitted for clarity. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Zn1-C4 1.9261(13), Zn2-C12 1.9307(13), Zn1-N1 2.1078(10), Zn1-N3 2.1768(11), Zn1-N4 2.0986(10), Zn2-N2 2.1055(11), Zn2-N3 2.0996(11), Zn2-N4 2.1524(10), N1-C3a 1.3065(15), N2-C2a 1.3111(16), N3-C2 1.3545(15), N4-C3 1.3578(15), C1-C2 1.5576(76), C1-C3 1.5649(15); N2a-C2-N3 137.21(12), N1a-C3-N4 137.26(11), C2-C1-C3 130.26(6), C2-C1-C2a 98.27(12), C2-C1-C3a 102.38(6), N1-Zn1-N3 101.34(4), N1-Zn1-N4 95.53(4), N3-Zn1-N4 83.43(4), N2-Zn2-N3 95.19(4), N2-Zn2-N4 100.62(4), N3-Zn2-N4 84.00(4).

Figure 4. Molecular structure of $\{C[C(Ni-Pr)_2ZnC\equiv CH]_4$ **5** (thermal ellipsoids are shown at 50% probability levels). H atoms except for $C\equiv CH$ ones are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn2-C32 1.926(3), Zn3-C34 1.949(3), C30-C31 1.171(4), C32-C33 1.183(4), Zn1-N1 2.127(2), Zn1-N2 2.130(2), Zn1-N8 2.116(2), Zn2-N1 2.127(2), Zn2-N2 2.124(2), Zn2-N3 2.095(2), N1-C4 1.352(3), N2-C2 1.354(2), N3-C3 1.314(2), N4-C2 1.303(3), C1-C3 1.555(3), C1-C2 1.567(3); N1-C4-N7 137.9(2), N3-C3-N5 137.7(2), C2-C1-C3 99.58(18), C2-C1-C4 130.43(19), C2-C1-C5 99.96(17), N1-Zn1-N2 83.43(8), N1-Zn1-N8 98.93(8), N2-Zn1-N8 97.54(8), N1-Zn2-N2 83.61(8), N1-Zn2-N3 97.60(8), N2-Zn2-N3 97.89(8).

SCHEME TITLES

Scheme 1. Synthesis of $\{C[C(Ni-Pr)_2ZnH]_4$ **3**. *i*-Pr groups bound to the N atoms are omitted for clarity; amidinato units containing a delocalized π -electron system are accentuated.

Scheme 2. Synthesis of **4** and **5**. *i*-Pr groups bound to the N atoms are omitted for clarity; amidinato units containing a delocalized π -electron system are accentuated.

TABLES

Table 2. Crystallographic details of **3**, **4**, and **5**.

	3	4	5
Empirical formula	C ₂₉ H ₆₀ N ₈ Zn ₄	C ₆₁ H ₇₆ N ₈ Zn ₄ *3[C ₄ H ₈ O]	C ₃₇ H ₆₀ N ₈ Zn ₄
Molecular mass	782.33 Da	1399.09	878.41
Space group	<i>C2/c</i>	<i>Pbcn</i>	P-1
T[K]	100(2)	100(2)	103(1)
λ [Å]	0.71073	0.71073	0.71073
a [Å]	11.1432(14)	16.7697(5)	10.6259(8)
b [Å]	18.004(2)	16.1494(5)	11.0517(8)
c [Å]	17.722(2)	25.9714(8)	18.1353(13)
α (°)	90	90	85.136(4)
β (°)	97.395(7)	90	89.363(4)
γ (°)	90	90	72.877(4)
V [Å ³]	3526.0(7)	7033.6(4)	2027.8(3)
Z	4	4	2
μ [mm ⁻¹]	1.399	4.503	2.373
D _{calcd.} [g cm ⁻³]	1.474	1.321	1.439
<i>R</i> 1 ^[a]	0.0246	0.0275	0.0291
<i>wR</i> 2 ^[b]	0.0582	0.0709	0.0671

^[a] $RI = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). - ^[b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ (for all data).

Figure 1

Figure 2

Figure 3

Figure 4

Scheme 1

Scheme 2

REFERENCES

- (1) For references, see: (a) Edelmann, F. T. *Chem. Soc. Rev.* **2009**, 38, 2253. (b) Edelmann, F. T. *Adv. Organomet. Chem.* **2008**, 57, 133. (c) Edelmann, F. T.; Coles, M. P. *Dalton Trans.* **2006**, 985. (d) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, 133, 219. (e) Cole, M. L. *Chem. Commun.* **2007**, 1579.
- (2) (a) Münch, M.; Flörke, U.; Bolte, M.; Schulz, S.; Gudat, D. *Angew. Chem.* **2008**, 120, 1535. *Angew. Chem. Int. Ed.* **2008**, 47, 1512. (b) Schmidt, S.; Gondzik, S.; Schulz, S.; Bläser, D.; Boese, R. *Organometallics* **2009**, 28, 4371.
- (3) Gutschank, B.; Schulz, S.; Westphal, U.; Bläser, D.; Boese, R. *Organometallics* **2010**, 29, 2093.
- (4) For references, see: Schulz, S.; Eisenmann, T.; Schuchmann, D.; Bolte, M.; Kirchner, M.; Boese, R.; Spielmann, J.; Harder, S. *Z. Naturforsch.* **2009**, 64b, 1397.
- (5) Marciniak, W.; Merz, K.; Moreno, M.; Driess, M. *Organometallics* **2006**, 25, 4931.
- (6) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin G. *Organometallics* **1995**, 14, 274.
- (7) Spielmann, J.; Piesik, D.; Wittkamp, B.; Jansen, G.; Harder, S. *Chem. Commun.* **2009**, 3455.
- (8) **4** was also synthesized by reaction of $\{C[C(Ni-Pr)_2ZnCl]_4\}$ **2a** with sodium phenylacetylide in THF (see experimental section method A).
- (9) Weiss, H.-C.; Bläser, D.; Boese, R.; Doughan, B. M.; Haley, M. M. *Chem. Commun.* **1997**, 1703.
- (10) Krieger, M.; Gould, R. O.; Neumüller, B.; Harms, K.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1998**, 624, 1434.
- (11) Fedushkin, I. L.; Eremenko, O. V.; Skatova, A. A.; Piskunov, A. V.; Fukin, G. K.; Ketkov S. Y. *Organometallics* **2009**, 28, 3863.
- (12) Prust, J.; Hohmeister, H.; Stasch, A.; Roesky, H. W.; Magull, J.; Alexopoulos, E.; Uson, I.; Schmidt, H. G.; Noltemeyer M. *Eur. J. Inorg. Chem.* **2002**, 2156.
- (13) Clegg, W.; Garcia-Alvarez, J.; Garcia-Alvarez, P.; Graham, D. V.; Harrington, R. W.; Hevia, E.; Kennedy, A. R.; Mulvey, R. E.; Russo, L. *Organometallics* **2008**, 27, 2654.

- (14) McMullan, R. K.; Kvik, A.; Popelier, P. *Acta. Cryst.* **1992**, *B48*, 726.
- (15) (a) Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem.* **1999**, *111*, 365. *Angew. Chem. Int. Ed.* **1999**, *38*, 354. (b) Root, D. M.; Landis, C. R.; Cleveland, T. *J. Am. Chem. Soc.* **1993**, *115*, 4201.
- (16) (a) Cremer, U.; Pantenburg, I.; Ruschewitz, U. *Inorg. Chem.* **2003**, *42*, 7716. (b) Cremer, U.; Ruschewitz, U. *Z Anorg. Allg. Chem.* **2004**, *630*, 337.
- (17) Jimenez, R.; Barral, M. C.; Moreno, V.; Santos, A. *J. Organomet. Chem.* **1979**, *182*, 353.
- (18) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.

TOC

The reaction of a tetranuclear amidinato zinc hydride $\{C[C(Ni-Pr)_2ZnH]_4$ **3**, which was obtained from the reaction of the corresponding Cl-substituted complex with CaH_2 , with two different acetylenes occurred with elimination of H_2 and subsequent formation of $\{C[C(Ni-Pr)_2ZnC\equiv CPh]_4$ **4** and $\{C[C(Ni-Pr)_2ZnC\equiv CH]_4$ **5**. **5** represents the first structurally characterized neutral zinc acetylene complex.

This text is made available via DuEPublico, the institutional repository of the University of Duisburg-Essen. This version may eventually differ from another version distributed by a commercial publisher.

DOI: 10.1021/om100966d

URN: urn:nbn:de:hbz:464-20201104-101948-8

This document is the Accepted Manuscript version of a Published Work that appeared in final form in: *Organometallics* 2010, 29, 22, 6133–6136, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see: <https://doi.org/10.1021/om100966d>

All rights reserved.