ORGANOMETALLICS
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Organometallics **2010,** *29,* 6133–6136 6133
DOI: 10.1021/om100966d

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

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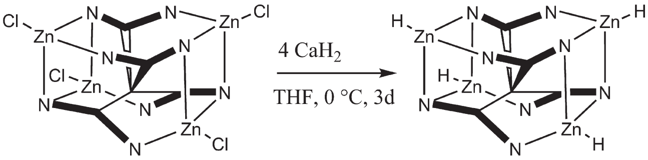
Received October 5, 2010

Summary: The tetranuclear amidinato zinc hydride complex $\{C[C(Ni\text{-}Pr)_2ZnH]_4\}$ (**3**) *was synthesized by reaction of the Cl-substituted complex* $\{C[C(Ni\text{-}Pr)_2ZnCl]_4\}$ *with* CaH_2. **3** *was found to react with phenylacetylene and acetylene at ambient temperature with elimination of* H_2 *and subsequent formation of* $C[C(Ni\text{-}Pr)_2ZnC{\equiv}CPh]_4$ (**4**) *and* $\{C[C(Ni\text{-}Pr)_2ZnC{\equiv}CH]_4$ (**5**)*, respectively.* **3**−**5** *have been characterized by multinuclear NMR (*^1H, ^{13}C*) and IR spectroscopy, elemental analyses, and single-crystal 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 amidinato 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 amidinato complexes such as $\{C[C(NR)_2ZnMe]_4\}$ ($R =$ *i*-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 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 toward hydrogen elimination reactions, insertion reactions, or addition reactions.

Scheme 1. Synthesis of $\{C[C(Ni\text{-}Pr)_2ZnH]_4$, **3**[a]



[a] *i*-Pr groups bound to the N atoms are omitted for clarity; amidinato units containing a delocalized π-electron system are accentuated.

Herein we report on the synthesis and crystal structure of $\{C[C(Ni\text{-}Pr)_2ZnH]_4$ (**3**). Moreover, initial studies on its reactivity toward 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 amidinato 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 complex containing covalently bound, terminal $C{\equiv}CH$ groups.

Results and Discussion

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

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 $\{C[C(Ni\text{-}Pr)_2ZnX]_4\}$.[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] proved 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 $[HZnOt\text{-}Bu]_4$ (1821 cm^{-1})[5] and [tris(3-*tert*-butylpyrazolyl)hydroborat]ZnH (1770 cm^{-1}).[6]

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

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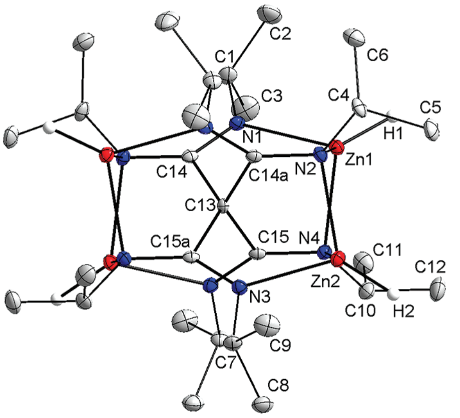
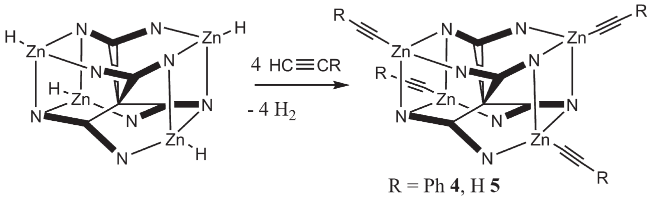


Figure 1. Molecular structure of $\{C[C(Ni\text{-}Pr)_2ZnH]_4$, **3** (thermal ellipsoids are shown at 50% probability levels). H atoms except for Zn−H ones are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zn1−H1 1.45(3), Zn2−H2 1.47(3), Zn1−N1 2.1273(17), Zn1−N2 2.1428(16), Zn1−N4 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).

Scheme 2. Synthesis of 4 and 5[a]



[a] *i*-Pr groups bound to the N atoms are omitted for clarity; amidinato units containing a delocalized π-electron system are accentuated.

*C*2/*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 amidinato groups, and the C−C bond lengths are in the range of typical C−C single bonds (1.559(0)−1.560(7) Å). The N−C bond lengths within the amidinato 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 amidinato groups and an additional H atom, adopt tetrahedral coordination spheres. The Zn−N bond lengths in **3** (2.1266(16)−2.1445(17) Å) are almost identical to those of **1a** and **2a**−**c**, and the Zn−H bond length (1.46(3) 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.

In order to evaluate the reactivity of the amidinato zinc hydride complex in more detail, **3** was reacted with HC≡CR (R = Ph, H) under mild reaction conditions (ambient temperature, acetylene at atmospheric pressure). These reactions almost quantitatively yielded the corresponding hydrogen elimination products $\{C[C(Ni\text{-}Pr)_2ZnC{\equiv}CPh]_4$ (**4**) and $\{C[C(NR)_2ZnC{\equiv}CH]_4$ (**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).

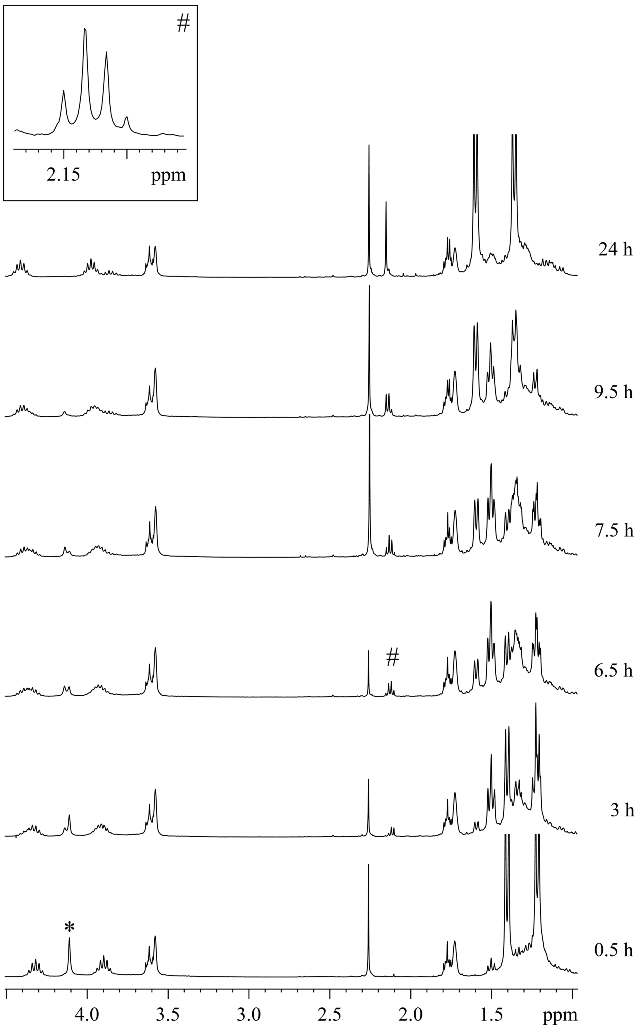


Figure 2. Time-dependent ^{1}H NMR monitoring of the reaction of **3** and HC≡CH in THF-D$_8$ (Zn−*H* indicated by *, Zn−C≡C*H* by #).

^{1}H NMR monitoring of the reaction of **3** and HC≡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 inset box in Figure 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 complex **5**.

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 $P\bar{1}$. Both complexes again

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(8) **4** was also synthesized by reaction of $\{C[C(Ni\text{-}Pr)_2ZnCl]_4\}$ (**2a**) with sodium phenylacetylide in THF (see Experimental Section, method A).

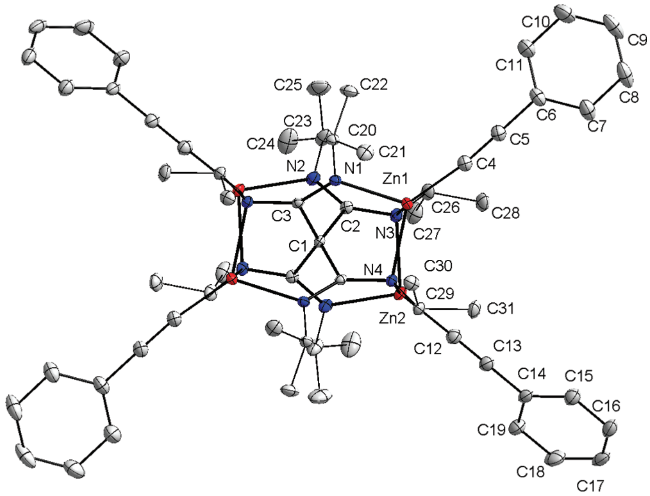

Figure 3. Molecular structure of $\{C[C(Ni\text{-}Pr)_2ZnC{\equiv}CPh]_4$, **4** (thermal ellipsoids are shown at 50% probability levels). H atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zn1−C4 1.9261(13), Zn2−C12 1.9307(13), Zn1−N1 2.1078(10), Zn1−N3 2.1768(11), Zn1−N4 2.0986(10), 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).

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 amidinato groups. The Zn atoms in **4** and **5** are tetrahedrally coordinated by three N atoms of adjacent amidinato 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 ethinyl 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 $[Zn(C{\equiv}CSiMe_3)(NPMe_3)]_4$ (1.20(2) Å), $[Zn(C{\equiv}C{-}C{\equiv}CSiMe_3)(NPEt_3)]_4$ (1.22(1) Å),[10] [(dpp-BIAN)Zn(μ-C≡CPh)]$_2$ (1.2099(17) Å),[11] and DippNacNacZnC≡CPh (1.207(3) Å),[12] as well as to the base-stabilized complex $(PhC{\equiv}C)_2Zn(tmeda)$ (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 140 K).[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 $[M([18]crown\text{-}6)(C{\equiv}CSiPh_3)_2]$ (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 164.2−175.5°.[13]

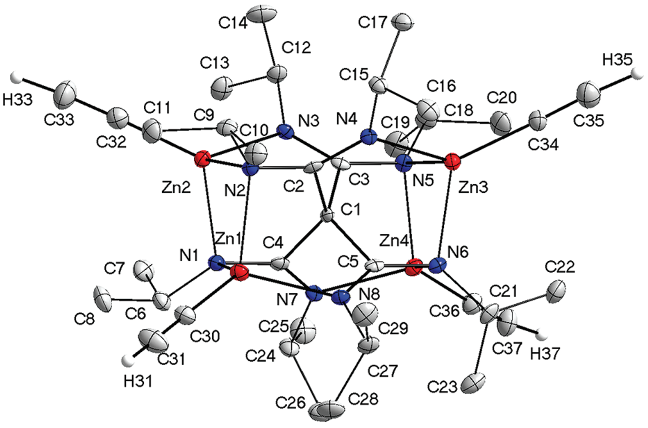

Figure 4. Molecular structure of $\{C[C(Ni\text{-}Pr)_2ZnC{\equiv}CH]_4$, **5** (thermal ellipsoids are shown at 50% probability levels). H atoms except for C≡CH ones are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Zn2−C32 1.926(3), Zn3−C34 1.949(3), C30−C31 1.171(4), C32−C33 1.183(4), 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).

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 $K_2Zn(C{\equiv}CH)_4{\cdot}2NH_3$ and $Rb_2Zn(C{\equiv}CH)_4$[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 $\{C[C(Ni\text{-}Pr)_2ZnC{\equiv}CPh]_4$ (**4**) and $\{C[C(Ni\text{-}Pr)_2ZnC{\equiv}CH]_4$ (**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

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Table 1. Crystallographic Details of 3, 4, and 5

	3	**4**	**5**
empirical formula	$C_{29}H_{60}N_8Zn_4$	$C_{61}H_{76}N_8Zn_4\cdot 3[C_4H_8O]$	$C_{37}H_{60}N_8Zn_4$
molecular mass	782.33 Da	1399.09	878.41
space group	*C*2/*c*	*Pbcn*	$P\bar{1}$
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 (deg)	90	90	85.136(4)
β (deg)	97.395(7)	90	89.363(4)
γ (deg)	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
R_1[a]	0.0246	0.0275	0.0291
wR_2[b]	0.0582	0.0709	0.0671

[a] $R_1 = \sum(\|F_o| - |F_c\|)/\sum|F_o|$ (for $I > 2\sigma(I)$). [b] $R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ (for all data).

were carefully dried over Na/K and degassed prior to use. **2a**[3] and sodium phenylacetylene[17] were prepared according to literature methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DMX 300 spectrometer and are referenced to internal C_6D_5H (^{1}H: $\delta = 7.154$; ^{13}C: $\delta = 128.0$), THF-D_8 (^{1}H: $\delta = 3.58, 1.73$), or $CDCl_3$ (^{1}H: $\delta = 7.26$; ^{13}C: $\delta = 77.0$). 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(N*i*-Pr)$_2$ZnH]$_4$}, 3. A 0.4 g (0.4 mmol) amount of **2a** and 0.04 g (0.9 mmol) of CaH_2 were suspended in 15 mL of THF, stirred for 3 days 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 $C_{29}H_{60}N_8Zn_4$ (782.48 g/mol): H, 7.06 (7.13); C, 44.44 (44.51); N, 14.21 (14.32). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.24 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.48 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 3.74 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$), 4.14 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$), 4.67 (s, 4 H, ZnH). ^{1}H NMR (300 MHz, THF-D_8, 25 °C): δ 1.22 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.41 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 3.90 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$), 4.67 (s, 4 H, ZnH), 4.32 (sept, 4 H, $^3J_{HH}$=6.4 Hz, CH(CH$_3$)$_2$). ^{13}C NMR (200 MHz, C_6D_6, 25 °C): δ 24.9 (*C*H$_3$), 25.6 (*C*H$_3$), 47.6 (*C*H), 48.9 (*C*H), 74.3 (*C*), 169.7 (N*C*N). 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(N*i*-Pr)$_2$ZnCCPh]$_4$}, 4. Method A: A solution of 0.25 g (0.27 mmol) of **2a** in 10 mL of THF was 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 and 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) of **3** and 0.5 mL (1 mmol) of phenylacetylene in 20 mL of THF was stirred for 3 h at 60 °C, yielding a yellowish solution, which 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 $C_{61}H_{76}N_8Zn_4$ (1182.95 g/mol): H, 6.41 (6.48); C, 61.64 (61.85); N, 8.50 (8.47). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.42 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.68 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 4.03 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$), 4.43 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(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 (*C*H$_3$), 24.8 (*C*H$_3$), 48.2 (*C*H), 49.8 (*C*H), 72.9 (*C*), 109.1 (ZnC*C*), 111.8 (Zn*C*C), 126.4 (*ipso*-C), 126.8 (*p*-C), 128.2 (*m*-C), 131.5 (*p*-C), 169.5 (N*C*N). 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(N*i*-Pr)$_2$ZnCCH]$_4$}, 5. A 0.4 g (0.5 mmol) sample of **3** was dissolved in 15 mL of THF and stirred for 1 day 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 $C_{37}H_{60}N_8Zn_4$ (878.57 g/mol): H, 6.81 (6.88); C, 50.63 (50.58); N, 12.61 (12.75). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.06 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.40 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.98 (s, 4 H, CCH), 3.47 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$), 3.85 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$). ^{1}H NMR (300 MHz, THF-D_8, 25 °C): δ 1.36 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 1.60 (d, 24 H, $^3J_{HH}$ = 6.4 Hz, CH(CH_3)$_2$), 2.15 (s, 4 H, CCH), 3.98 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$), 4.41 (sept, 4 H, $^3J_{HH}$ = 6.4 Hz, CH(CH$_3$)$_2$). ^{13}C NMR (200 MHz, C_6D_6, 25 °C): δ 24.2 (*C*H$_3$), 24.8 (*C*H$_3$), 48.2 (*C*H), 50.0 (*C*H), 63.8 (*C*), 96.7 (ZnC*C*H), 106.5 (Zn*C*CH), 169.9 (N*C*N). 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 an APEX2 detector using monochromated Mo Kα radiation. Crystallographic data for **3**, **4**, and **5** are summarized in Table 1. Absorption corrections were performed semiempirically from equivalent reflections on the basis of multiscans (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 rigid 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** indicates 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 nos. CCDC-790554 (**3**), -790555 (**4**), and -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.S. thanks the German Science Foundation (DFG) for financial support.

Supporting Information Available: 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.

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