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Synthesis and Crystal Structures of *t*-Butyl-Pyridine Adducts of ZnR_2 ($\text{R} = \text{Me}, i\text{-Pr}, t\text{-Bu}, \text{Cp}^*$)

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Abstract. Lewis acid-base adducts of the general type $\text{R}_2\text{Zn}(4\text{-}t\text{-BuPy})_x$ ($\text{R} = \text{Me}$ **1**, *i*-Pr **2**, *t*-Bu **3**, Cp^* **4**; $x = 1, 2$) were obtained in high yields from reactions of ZnR_2 with the Lewis base 4-*t*-Bu-Pyridine. **1** - **4** were

characterized by multinuclear NMR (^1H , ^{13}C) and IR spectroscopy and elemental analyses, **1** and **4** also by X-ray diffraction at single crystals.

Keywords: Zinc, Lewis acid, Lewis base, X-Ray Structures

Introduction

Metal organic complexes MR_x of group 2 (Be, Mg), 12 (Zn) and 13 metals (Al, Ga) are typically used as alkylating reagents in organic and organometallic chemistry.[1] When compared to each other, zinc alkyls were found to be the less reactive species within this series but, as a consequence, they are the most selective agents.[2] Moreover, their high tolerance toward functional groups renders them very valuable in organic synthesis.[3] A second reaction pattern these complexes have in common is their reactivity as Lewis acid. Group 2 and group 13 organometallic complexes typically exhibit a rather strong Lewis acidity, whereas organozinc complexes are rather weak Lewis acids, most likely due to the presence of a filled *d* shell. The methyl complexes clearly reflect this trend as can be seen when comparing their solid state structures. BeMe_2 , MgMe_2 and AlMe_3 compensate their electron deficiency by forming 2-electron-3-center bonds, hence forming endless chains (Be, Mg) or dimeric complexes (Al) in the solid state, whereas ZnMe_2 is a monomeric complex.[4] As a consequence, group 2 and 13 metals rather form strong Lewis acid-base adducts with σ -donors such as amines NR_3 and phosphines PR_3 , whereas the corresponding zinc complexes are rather weak.

Although Lewis acid-base-adducts of organozinc complexes are already known for about 50 years,[5] the interest in these complexes has increased over the last two decades due to their potential applications as precursors in metal organic chemical vapor deposition (MOCVD).[6] Moreover, Lewinski *et al.* reported very recently on reactions of dialkylzinc adducts of the type $[\text{ZnR}_2(\text{L})_2]$, which were found to activate O_2 by formation of zinc alkylperoxides LZn(R)OOR . [7] Even more remarkable is the synthesis of the adduct $[\text{t-Bu}_2\text{Zn}(\text{bpe})]$ ($\text{bpe} = 1,2\text{-bis(4-pyridyl)-ethane}$), which forms a 2D framework in the solid state that is without precedence in organozinc chemistry.[8] This finding was rather unexpected

since zinc alkyls typically form adducts of the type R_2ZnL and R_2ZnL_2 ($\text{L} = \sigma\text{-donor}$), respectively, in which the central Zn atom either adopt trigonal planar or distorted tetrahedral coordination spheres.[9] Sterical interaction between the organic substituents and the Lewis base were reported to play a crucial role on the resulting coordination geometry of the central Zn atom.[9a, 6b, 10]

Scheme 1. Typical coordination modes of ZnR_2 adducts.

Due to our long term interest in Lewis acid-base reactions of main group metal [11] and transition metal complexes [12], we became interested in reactions of dialkylzinc complexes with strong σ -donors, in particular pyridine-based donors. Herein, we report on the synthesis and crystal structures of several Lewis acid-base adducts of different zinc dialkyls ZnR_2 ($\text{R} = \text{Me}, n\text{-Pr}, i\text{-Pr}, t\text{-Bu}$) as well as zincocene Cp^*_2Zn with the strong Lewis base 4-*tert*-butyl-pyridine (4-*t*-BuPy).

Experimental Section

General Procedure

All manipulations were performed in a glovebox under an N_2 atmosphere or with standard Schlenk techniques. Solvents were dried over sodium/potassium or by use of a solvent purification system (MBRAUN) and degassed prior to use. ZnMe_2 (4 mmol, 2M in Toluol) and 4-*t*-BuPy are commercially available from Acros. ZnR_2 ($\text{R} = i\text{-Pr}, t\text{-Bu}$) [13] and Cp^*_2Zn [14] were prepared as described in the literature. A Bruker Avance 300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$) and IR spectra using an ALPHA-T FT-IR spectrometer equipped with an ATR unit. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Duisburg-Essen.

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General Synthesis of (4-*t*-BuPy)₂ZnR₂ (R = Me, *i*-Pr, *t*-Bu): 1.22 g (9 mmol) 4-*t*-BuPy was added to a solution of 2 mmol of the corresponding dialkylzinc ZnR₂ in 10 mL of *n*-pentane, stirred for 1 h at ambient temperature and then stored at -30 °C, yielding colorless crystals of **1** – **3**. Yields are given for the isolated crystalline materials.

(4-*t*-BuPy)₂ZnMe₂ 1: Yield 0.57 g (71 %). Mp: 62 °C. Anal. C₂₀H₃₂N₂Zn (365.88 g/mol): found (calcd): H 8.7 (8.8); C 65.1 (65.7); N 7.5 (7.7); Zn 16.8 (17.9). ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ -0.13 (s, 6 H, ZnMe₂), 0.96 (s, 18 H, CMe₃), 6.75 (dd, ³J_{HH} = 4.4 Hz, ³J_{HH} = 1.9 Hz, 4 H, C(3)–H), 8.42 (dd, ³J_{HH} = 4.4 Hz, ³J_{HH} = 1.6 Hz, 4 H, C(2)–H). ¹³C-NMR (75 MHz, 25 °C, C₆D₆): δ -1.3 (ZnMe₂), 30.1 (CMe₃), 34.2 (CMe₃), 120.8 (C(3)), 149.8 (C(2)), 163.5 (C(4)). IR: ν 2965, 2909, 2881, 2810, 1604, 1496, 1413, 1366, 1260, 1222, 1145, 1072, 1010, 828, 799, 633, 569, 515, 465 cm⁻¹.

(4-*t*-BuPy)₂Zn(*i*-Pr)₂ 2: Yield 0.80 g (68 %). Mp: 66 °C. Anal. C₂₄H₄₀N₂Zn (421.98 g/mol): found (calcd): H 9.4 (9.6); C 68.1 (68.3); N 6.7 (6.6); Zn 17.2 (15.5). ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ 0.95 (s, 18 H, CMe₃), 1.00 (m, 2 H, Me₂CH), 1.62 – 1.64 (d, ³J_{HH} = 7.8 Hz, 12 H, Me₂CH), 6.77 (dd, ³J_{HH} = 4.1 Hz, ³J_{HH} = 1.6 Hz, 4 H, C(3)–H), 8.38 (dd, ³J_{HH} = 4.7 Hz, ³J_{HH} = 1.9 Hz 4 H, C(2)–H). ¹³C-NMR (75 MHz, 25 °C, C₆D₆): δ 16.2 (Me₂CH), 23.9 (Me₂CH), 30.2 (CMe₃), 34.4 (CMe₃), 121.0 (C(3)), 149.6 (C(2)), 160.2 (C(4)). IR: ν 2965, 2926, 2908, 2868, 2794, 2688, 1605, 1546, 1497, 1458, 1414, 1366, 1273, 1222, 1070, 1011, 937, 866, 842, 829, 719, 570, 537, 490, 466 cm⁻¹.

(4-*t*-BuPy)₂Zn(*t*-Bu)₂ 3: Yield 0.53 g (59 %). Mp: 77 °C. Anal. C₂₆H₄₄N₂Zn (450.05 g/mol): found (calcd): H 9.7 (9.9); C 68.6 (69.4); N 6.1 (6.2); Zn 16.6 (14.5). ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ 0.95 (s, 18 H, CMe₃), 1.39 (s, 18 H, CMe₃), 6.78 – 6.80 (dd, ³J_{HH} = 4.4 Hz, ³J_{HH} = 1.7 Hz, 4 H, C(3)–H), 8.37 – 8.39 (dd, ³J_{HH} = 4.4 Hz, ³J_{HH} = 1.6 Hz, 4 H, C(2)–H). ¹³C-NMR (75 MHz, 25 °C, C₆D₆): δ 24.8 (Zn(CMe₃)₂), 30.3 (CMe₃), 34.3 (CMe₃), 34.7 (Zn(CMe₃)₂), 120.7 (C(3)), 150.2 (C(2)). IR: ν 2967, 2929, 2907, 2776, 2735, 2678, 1608, 1458, 1415, 1366, 1274, 1224, 1072, 1007, 826, 808, 720, 569, 538, 497, 392 cm⁻¹.

Synthesis of 4-*t*-BuPy-ZnCp*₂ 4: A solution containing 0.67 g Cp*₂Zn (2.0 mmol) and 0.68 g 4-*t*-BuPy (5 mmol) in 20 mL of *n*-hexane were stirred for 1 h at ambient temperature, concentrated to 10 mL and then stored at -30 °C. Colorless crystals were formed within 36 h. Yield 0.86 g (91%). Mp: 107 °C. Anal. C₂₉H₄₃NZn (471.05 g/mol): found (calcd): H 9.1 (9.2); C: 73.2 (73.9); N, 3.1 (3.0); Zn, 13.9 (13.9). ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ 0.93 (s, 9H, CMe₃), 1.95 (s, 30 H, C₅Me₅), 6.68 (dd, ³J_{HH} = 4.7 Hz, ³J_{HH} = 1.6 Hz, 2 H, C(3)–H), 7.87 (dd, ³J_{HH} = 4.4 Hz, ³J_{HH} = 1.6 Hz, 2 H, C(2)–H). ¹³C{¹H}-NMR (125 MHz, C₆D₆, 25 °C): δ 11.7 (C₅Me₅), 30.1 (CMe₃), 34.5 (CMe₃), 113.3 (C₅Me₅), 120.1 (C(3)), 148.5 (C(2)), 160.8 (C(4)). IR: ν 2957, 2902, 2848, 1614, 1420, 1370, 1315, 1275, 1229, 1077, 1026, 937, 826, 793, 728, 634, 571, 409 cm⁻¹.

X-ray Structure Solution and Refinement. Crystallographic data of **1** and **4** are given in Table 1, bond lengths and angles for **1** and **4** are summarized in Table 2. Figures 1 and 2 show ORTEP diagrams of the solid state structures of **1** and **4**. Data were collected on a Bruker-AXS SMART APEX CCD. The structures were solved by Direct Methods (SHELXS-97) [15] and refined by full-matrix least-squares on F² (SHELXL-97).[16] Semi-empirical absorption corrections were applied for **1** and **4**. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. The crystallographic data of **1** and **4** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-648547 (**1**) and CCDC-644934 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (Telefax: (+44) 1223/336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic details for **1** and **4**.

	1 ^[d]	4 ^[e]
empirical formula	C ₂₀ H ₃₂ N ₂ Zn	C ₂₉ H ₄₃ NZn x (C ₇ H ₈)
molecular mass	365.85	563.15
cryst syst	monoclinic	orthorhombic
space group	Pc	Imm2
a [Å]	10.0765(6)	9.4421(3)
b [Å]	17.8134(11)	13.5309(4)
c [Å]	11.3793(7)	13.1884(4)
β [deg]	92.819(3)	

V [Å ³]	2040.1(2)	1684.95(9)
Z	4	2
T [K]	100(1)	153(1)
radiation (λ [Å])	Mo-Kα (0.71073)	Mo-Kα (0.71073)
μ [mm ⁻¹]	1.206	0.751
D _{calc} [g cm ⁻³]	1.191	1.110
2θ _{max} [deg]	54.16	50.26
cryst dimens [mm]	0.26 x 0.26 x 0.15	0.32 x 0.25 x 0.18
no. of reflns	28463	10188
no. of unique reflns	8195	1657
R _{merg}	0.0287	0.0204
no. of param.	415 / 2	116 / 1
refined/restraints		
R1 ^[a]	0.0300	0.0234
wR2 ^[b]	0.0724	0.0603
goodness of fit ^[c]	1.038	0.973
final max/min. Δρ, e Å ⁻³	0.682 / -0.339	0.205 / -0.164

^[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$ (for $I > 2\sigma(I)$). - ^[b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. -

^[c] Goodness of fit = $\{\sum[w(F_o^2 - F_c^2)^2]/(\text{No.observs} - \text{N.params})\}^{1/2}$. - ^[d] ADP's of C(18-20)

show severe disorder which could not be resolved. Consequently, atom distances given for these atoms have no significance. Zn atoms and methyl groups are fitted with weighted R.M.S. deviation 0.0235 Å. - ^[e] *t*-Bu carbon atoms C(6) and C(7) are disordered over two sites with SOF 0.5 together with the riding hydrogen atoms. The methyl hydrogen atoms of the toluene molecule are also disordered over two sites with SOF 0.5. The absolute structures of **1** and **4** were determined (Flack parameter 0.014(8) **1**, 0.044(13) **6**).[17]

Table 2. Selected bond lengths [Å] and angles [°] of **1** and **4**.

	1 ^[a]		4
Zn1-N1 / N11	2.214(2) / 2.214(2)	Zn1-N1	2.019(3)
Zn1-C21 / C22	1.994(2) / 2.005(2)	Zn1-C8 / C9	2.074(3) / 2.553(2)
N1-C2 / C6	1.331(3) / 1.330(3)	N1-C2	1.331(3)
C3-C2 / C4	1.382(3) / 1.391(3)	C3-C2 / C4	1.377(4) / 1.385(3)
C4-C5 / C7	1.388(3) / 1.525(3)	C4-C5	1.536(4)
C5-C6	1.380(3)		
N1-Zn1-C21	102.57(10)	N1-Zn1-C8	116.67(8)
N1-Zn1-C22	102.79(9)	N1-Zn1-C9	94.44(6)
N11-Zn1-C21	102.65(9)		
N11-Zn1-C22	103.42(9)		
N1-Zn1-N11	97.09(7)		
C21-Zn1-C22	140.72(11)		

^[a] Structural parameters are only given for Zn1, whereas those of Zn2 can be found in the CCDC-file.

Results and Discussion

ZnR₂ (R = Me **1**, *i*-Pr **2**, *t*-Bu **3**, Cp* **4**) were reacted with an excess of 4-*t*-BuPy in *n*-pentane and the resulting Lewis acid-base adducts were obtained as colorless crystalline solids after storage at -30 °C.

R = Me **1**, *i*-Pr **2**, *t*-Bu **3**, x = 2; R = Cp* **4**, x = 1

Scheme 2. Synthesis of Lewis acid-base adducts **1** – **4**.

¹H and ¹³C NMR spectra of **1** – **4** in C₆D₆ show typical sets of resonances due to the substituents R and the Lewis base 4-*t*-BuPy in the expected 1:2 (**1** – **3**) and 1:1 (**4**) molar ratios, indicating the

formation of the corresponding bis-adducts $(4\text{-}t\text{-BuPy})_2\text{ZnR}_2$ (**1** – **3**) and mono-adduct $(4\text{-}t\text{-BuPy})\text{ZnCp}^*_2$ (**4**), respectively.

Figure 1. Molecular structure and atom numbering scheme of **1**; thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Figure 2. Molecular structure and atom numbering scheme of **4**; thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

The solid-state structures of compounds **1** and **4** were determined by single crystal X-ray diffraction. Suitable crystals were obtained from solutions in *n*-pentane after slow crystallization at $-30\text{ }^{\circ}\text{C}$. **1** crystallizes in the monoclinic space group *Pc* with two independent molecules in the elemental cell and **4** in the orthorhombic space group *Imm*2. The central Zn atom in **1** is coordinated by two Lewis bases, hence adopting a distorted tetrahedral coordination sphere. The C–Zn–C angle in **1** (140.7°) is distorted by almost 40° compared to the linear geometry of the parent alkyl ZnMe_2 as is typical for Lewis base-adducts of zinc dialkyls. The extent of distortion typically relates to the rigidity, the coordination number of the central zinc atom and the steric demand of the coordinating Lewis

bases and the organic substituents R of the organozinc unit.[9c,f, 6b, 18] Due to the expressed steric demand of the bulky Cp^*_2Zn only coordinates a single 4-*t*-BuPy molecule. As a consequence, the Zn atom in **4** adopts a trigonal planar coordination sphere as was observed in the corresponding 4-dimethylaminopyridine (dmap) adduct $\text{Cp}^*_2\text{Zn-dmap}$,[9a] which belongs to the rather rare structurally characterized Lewis acid-base adducts of the type R_2ZnL with neutral ligands L. This type of complexes is typically observed in alkyl(amido)zincates.[9b, 19] Both Cp^* substituents in **4** are η^3 -bonded to the central Zn atom (Zn1-C8 2.074(3); Zn1-C9 2.553(2) Å), whereas a η^2 -coordination was observed in $\text{Cp}^*_2\text{Zn(dmap)}$ (2.090(5) – 2.483(5) Å). The Zn–C bond lengths in **1** (Zn1-C21 1.994(2), Zn1-C22 2.005(2) Å) are also comparable to those of the corresponding dmap adduct $\text{Me}_2\text{Zn(dmap)}_2$ (Zn–C 2.022(2) – 2.023(2) Å).[12a] The coordination of the Zn atom by the Lewis base causes only a small increase in the zinc carbon bond length in comparison to the non-coordinated organozinc derivatives (ZnMe_2 : 1.930(2) Å; Cp^*_2Zn : 2.04 – 2.28 Å),[14, 20] indicating a rather low weakening of the Zn–C bond. A comparison of the Zn–N bond lengths in the 4-*t*-BuPy adduct **1** (Zn1-N1 2.214(2), Zn1-N11 2.214(2) Å) and the corresponding dmap adduct $\text{Me}_2\text{Zn(dmap)}_2$ (Zn1-N1/2 2.177(2) Å) shows no significant difference. The same finding is observed when comparing **4** (Zn1-N1 2.019(3) Å) and $\text{Cp}^*_2\text{Zn(dmap)}$ (Zn1-N1 2.024(3) Å). In contrast the Zn–N bond lengths observed in the base stabilized Zn(I) complex $\text{Cp}^*_2\text{Zn}_2(\text{dmap})_2$ (Zn2-N1 2.115(2), Zn2-N3 2.125(2) Å) are significantly elongated.[9a] Nevertheless, the Zn–N bond lengths in **1** and **4** are within the sums of the van der Waals radii.[21] An evaluation of the Cambridge Structural Database System shows that Zn–N bond lengths typically range from 2.02 to 2.28 Å for threefold-coordinated (R_2ZnL) and tetrahedral-coordinated Zn atoms (R_2ZnL_2), respectively. Only the adducts $\text{Me}_2\text{Zn}\{\text{CH}_2\text{NMe}\}_3$ (Zn-N 2.42 Å) [9c] and $(\text{Me}_3\text{CCH}_2)_2\text{Zn(tmeda)}$ (Zn-N 2.41 Å) [6b] exhibit significantly longer Zn–N bond lengths.

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References

- [1] J. T. B. H. Jastrzebski, J. Boersma, G. Van Koten, *Structural organozinc chemistry*, John Wiley & Sons, Ltd, **2007**.
- [2] W. Carruthers, I. Coldham, *Modern Methods of Organic Synthesis*, 4. Ed., Cambridge University Press, **2004**.
- [3] a) P. Knochel, R. D. Singer, *Chem. Rev.* **1993**, *93*, 2117; b) P. Knochel, J. J. A. Perea, P. Jones, *Tetrahedron* **1998**, *54*, 8275.
- [4] a) J. P. Oliver, *Adv. Organomet. Chem.* **1977**, *15*, 235; b) A. F. Holleman, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 102. Ed., Walter de Gruyter, **2007**;
- [5] K.-H. Thiele, *Z. Anorg. Allg. Chem.* **1962**, *319*, 183; b) K.-H. Thiele, *Z. Anorg. Allg. Chem.* **1963**, *322*, 71.
- [6] a) M. B. Hursthouse, M. Motevalli, P. O'Brien, J. R. Walsh, *Organometallics* **1991**, *10*, 3196; b) P. O'Brien, M. B. Hursthouse, M. Motevalli, J. R. Walsh, A. C. Jones, *J. Organomet. Chem.* **1993**, *449*, 1.
- [7] J. Lewinski, W. Sliwinski, M. Dranka, I. Justyniak, J. Lipkowski, *Angew. Chem.* **2006**, *118*, 4944; *Angew. Chem. Int. Ed.* **2006**, *45*, 4826.
- [8] J. Lewinski, M. Dranka, W. Bury, W. Sliwinski, I. Justyniak, J. Lipkowski, *J. Am. Chem. Soc.* **2007**, *129*, 3096.
- [9] a) D. Schuchmann, U. Westphal, S. Schulz, U. Flörke, D. Bläser, R. Boese, *Angew. Chem.* **2009**, *121*, 821; *Angew. Chem. Int. Ed.* **2009**, *48*, 807; b) D. V. Graham, E. Hevia, A. R. Kennedy, R. E. Mulvey,

- Organometallics* **2006**, *25*, 3297; c) M. B. Hursthouse, M. Motevalli, P. O'Brien, J. R. Walsh, A. C. Jones, *J. Mater. Chem.* **1991**, *1*, 139; d) H. Mimoun, J. Y. de Saint Laumer, L. Giannini, R. Scopelliti, C. Floriani, *J. Am. Chem. Soc.* **1999**, *121*, 6158; e) A. Johansson, E. Wingstrand, M. Håkansson, *J. Organomet. Chem.* **2005**, *690*, 3846; f) A. Lennartson, A. Hedström, M. Håkansson, *Acta Cryst.* **2007**, *E63*, 123; g) J. Krahmer, R. Beckhaus, W. Saak, D. Haase, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1696; h) M.-L. Cheng, H.-X. Li, L.-L. Liu, H.-H. Wang, Y. Zhang, J.-P. Lang, *Dalton Trans.* **2009**, 2012.
- [10] A. Kuczkowski, S. Schulz, M. Nieger, P. R. Schreiner, *Organometallics* **2002**, *21*, 1408.
- [11] a) F. Thomas, T. Bauer, S. Schulz, M. Nieger, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2018; b) A. Kuczkowski, S. Fahrenholz, S. Schulz, M. Nieger, *Organometallics* **2004**, *23*, 3615; c) S. Schulz, F. Thomas, W. Priesmann, M. Nieger, *Organometallics* **2006**, *25*, 1392; d) S. Schulz, *Coord. Chem. Rev.* **2001**, *215*, 1; e) S. Schulz, *Adv. Organomet. Chem.* **2003**, *49*, 225.
- [12] a) F. Thomas, S. Schulz, M. Nieger, *Angew. Chem.* **2005**, *117*, 5813; *Angew. Chem. Int. Ed.* **2005**, *44*, 5668; b) S. Schulz, M. Münch, U. Flörke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2221.
- [13] a) A. Boudier, C. Darcel, F. Flachsmann, L. Micouin, M. Oestreich, P. Knochel, *Chem. Eur. J.* **2000**, *6*, 2748; b) H. Lehmkuhl, O. Olbrysch, *Liebigs Ann. Chem.* **1975**, 1162.
- [14] R. Blom, J. Boersma, P. H. M. Budzelaar, B. Fischer, A. Haaland, H. V. Volden, J. Weidlein, *Acta Chemica Scandinavica* **1986**, *A 40*, 113.
- [15] G. M. Sheldrick, SHELXS-97, Program for Structure Solution: *Acta Crystallogr. Sect. A*, 1990, *46*, 467.
- [16] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, 1997.
- [17] H. D. Flack, *Acta Cryst.* 1983, *A39*, 876-881.
- [18] M. Motevalli, P. O'Brien, A. J. Robinson, J. R. Walsh, P. B. Wyatt, *J. Organomet. Chem.* **1993**, *461*, 5.
- [19] For examples see: a) P. C. Andrikopoulos, D. R. Armstrong, H. R. L. Barley, W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, *J. Am. Chem. Soc.* **2005**, *127*, 6184; b) M. Uchiyama, Y. Matsumoto, D. Nobuto, T. Furuyama, K. Yamaguchi, K. Morokuma, *J. Am. Chem. Soc.* **2006**, *128*, 8748; c) W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, R. E. Mulvey, *Angew. Chem.* **2006**, *118*, 2430; *Angew. Chem. Int. Ed.* **2006**, *45*, 2370; d) W. Clegg, S. H. Dale, E. Hevia, L. M. Hogg, G. W. Honeyman, R. E. Mulvey, C. T. O'Hara, *Angew. Chem.* **2006**, *118*, 6698; *Angew. Chem. Int. Ed.* **2006**, *45*, 6548; e) B. Conway, D. V. Graham, E. Hevia, A. R. Kennedy, J. Klett, R. E. Mulvey, *Chem. Commun.* **2008**, 2638; f) W. Clegg, D. V. Graham, E. Herd, E. Hevia, A. R. Kennedy, M. D. McCall, L. Russo, *Inorg. Chem.* **2009**, *48*, 5320; g) W. Clegg, B. Conway, D. V. Graham, E. Hevia, A. R. Kennedy, R. E. Mulvey, L. Russo, D. S. Wright, *Chem. Eur. J.* **2009**, *15*, 7074.
- [20] A. Almenningen, T. U. Helgaker, A. Haaland, S. Samdal, *Acta Chem. Scand.* **1982**, *36A*, 159.
- [21] a) A. Bondi, *J. Phys. Chem.* **1966**, *70*, 3006; b) S. S. Batsanov, *J. Mol. Struct.* **1999**, *468*, 151; c) S. Nag, K. Banerjee, D. Datta, *New J. Chem.* **2007**, *31*, 832.

TOC entry

Synthesis and Crystal Structures of *t*-Butyl-Pyridine Adducts of ZnR_2 ($\text{R} = \text{Me}, i\text{-Pr}, t\text{-Bu}, \text{Cp}^*$)

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Lewis acid-base adducts of the general type $\text{R}_2\text{Zn}(4\text{-}t\text{-BuPy})_x$ were obtained from reactions of ZnR_2 with the strong Lewis base 4-*tert*-Butylpyridine.

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