Synthesis of 1,4-Diamino-2,3-di(2-pyridyl)butane and its Dinuclear Zinc(II) Chloride Complex

Tobias Kloubert, Martin Schulz, Helmar Görls, Manfred Friedrich, and Matthias Westerhausen

Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, August-Bebel-Straße 2, 07743 Jena, Germany

Reprint requests to Prof. M. Westerhausen. Fax: +49 (0) 3641 948102. E-mail: m.we@uni-jena.de

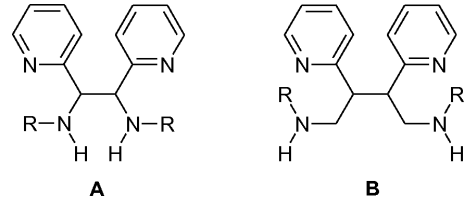
Z. Naturforsch. **2009**, *64b,* 784 – 792; received March 9, 2009

In a Henry-type reaction nitromethane reacts with *N*-(2-pyridylmethylidene)-methylamine (**1**) yielding 1-methylamino-1-(2-pyridyl)-2-nitromethane (**2**) in nearly quantitative yield. This orange compound decomposes slowly in an inert gas atmosphere and fast in contact with air. Therefore **2** has to be stored at −78 °C as a methanol solution. Reduction of **2** with hydrogen in the presence of a Pd/C catalyst leads to the formation of 1,4-dinitro-2,3-di(2-pyridyl)butane (**3**) in the rather poor yield of 12 %. The major product is the *meso*-isomer, *meso*-**3**, whereas only traces of (*R*,*R*)- and (*S*,*S*)-isomers of **3** are formed. A conversion of the nitro groups into amino functionalities succeeds with hydrazine hydrate in the presence of a Pd/C catalyst yielding *meso*-1,4-diamino-2,3-di(2-pyridyl)butane (**4**). Recrystallization from an aqueous solution gives **4**·2H_2O. The zinc(II) chloride complex **5** with the metal atoms in distorted tetrahedral environments can be isolated after addition of two equivalents of $ZnCl_2$ to **4**. The molecular structures of trimeric **1**, *meso*-**3**, (*R*,*R*)/(*S*,*S*)-**3**, *meso*-**4**, and **5** have been determined and are discussed.

Key words: Chelate Bases, Amines, Nitro Compounds, Zinc Complexes, Reduction Reactions

Introduction

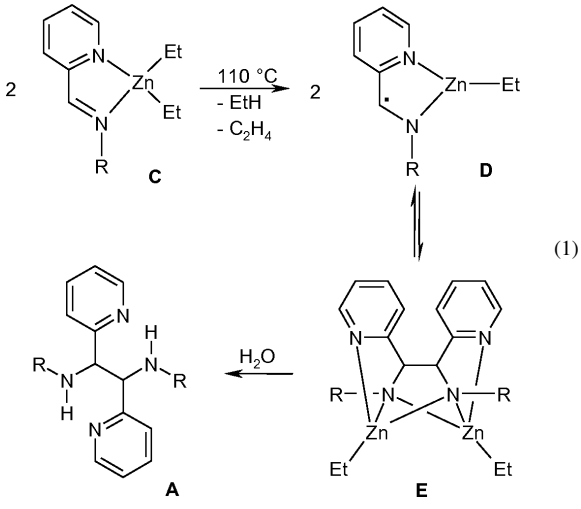
Vicinal diamines represent widely used bidentate Lewis bases. In order to enhance the denticity, 2-pyridyl groups can be bound to these diaminoethanes giving *e. g.* 1,2-diamino-1,2-di(2-pyridyl)ethane **A** (Scheme 1). In contrast to these widely used ligands, 1,4-diamino-2,3-di(2-pyridyl)butanes **B** with a larger bite (N···N distance) are unknown as of yet. Several reaction routes can be employed for the synthesis of the 1,2-diamino-1,2-di(2-pyridyl)ethane derivatives **A**. Unsubstituted 1,2-diamino-1,2-di(2-pyridyl)ethane **A** (R = H) has been shown to be available in good yield from a [3.3]-sigmatropic rearrangement of a diimine with subsequent hydrolysis [1, 2]. Another pathway started from *N*-(2-pyridylmethylidene)-alkylamines which were coupled *via* irradiation with a medium-pressure mercury lamp and treated with $NaHCO_3$ yielding 1,2-di(alkylamino)-1,2-di(2-pyridyl)ethanes **A** (R = *n*Hex, *c*Pr, *c*Hex, Ph_2CH) [3]. The reductive coupling of imines with aluminum or bismuth in methanol in the presence of KOH also gave vicinal diamines [4]. A variant of this reaction employed a mixture of zinc and chloro-trimethylsilane as reducing agents and allowed the synthesis of **A**

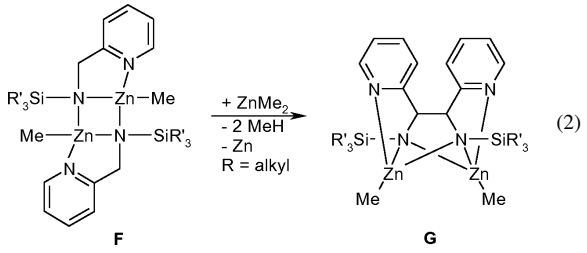


Scheme 1. Tetradentate amino bases **A** and **B**.

(R = Me) [5] whereas lithium is not a suitable reducing reagent if pyridyl groups are present in the molecules [6]. Low-valent titanium species, produced from $TiCl_4$ and magnesium amalgam, were also able to reductively couple *N*-(2-pyridylmethylidene)-methylamine [7]. Treatment of *N*-(2-pyridylmethylidene)-1-phenylethylamine with methyllithium gave mainly the addition product, but derivative **A** (R = CH(Me)Ph) was obtained as a by-product [8].

The reductive coupling with metal-containing reagents often led to the formation of metal complexes with the deprotonated 1,2-diamino-1,2-di(2-pyridyl)ethanes **A**. The reaction of *N*-(2-pyridylmethylidene)-*tert*-butylamine with "gallium(I) iodide" yielded [bis{diiodo gallium(III)} 1,2-di(*tert*-butylamido)-1,2-di(2-pyridyl)ethane] [9]. A coupling





of imines could also be promoted by SmI_2 and Lewis acids allowing an efficient stereoselective synthesis of C_2-symmetric 1,2-diamines [10]. A metal-mediated reductive coupling of *N*-(2-pyridylmethylidene)-alkylamines with $Ru_3(CO)_{12}$ yielded the ruthenium complex of 1,2-di(alkylamido)-1,2-di(2-pyridyl)ethane (R = *i*Pr, *t*Bu, *c*Hex) [11, 12]. At elevated temperatures the complex {*N*-(2-pyridylmethylidene)-*tert*-butylamine}diethylzinc **C** liberated ethane and ethene giving [bis(ethylzinc) 1,2-di(*tert*-butylamido)-1,2-di(2-pyridyl)ethane] (**E**) [13, 14] which showed an equilibrium with its monomer **D** *via* C–C bond cleavage, as shown in Eq. 1 [15]. This interesting monomer-dimer equilibrium, which involves C–C bond cleavage and C–C bond formation was studied in detail thereafter [16, 17]. Hydrolytic work-up procedures led to the formation of 1,2-di(*tert*-butylamino)-1,2-di(2-pyridyl)ethane **A** (R = *t*Bu) [15].

The oxidative C–C coupling of 2-pyridylmethylamine also led to the formation of various by-products [18]. Protection of the amino functionalities by trialkylsilyl groups led to a quantitative formation of the C–C coupled product [di(methylzinc) 1,2-di(2-pyridyl)-1,2-bis(trialkylsilylamido)ethane] **G**, as shown in Eq. 2 [19, 20]. The protolysis of this zinc complex with acetamide gave 1,2-di(2-pyridyl)-1,2-bis(trialkylsilylamino)ethanes **A** (R = SiR'_3) in good yield whereas hydrolysis also cleaved the N-Si bonds [21]. A variant of this method resembled the oxidative C–C coupling of dilithium (2-pyridylmethanidyl)(*tert*-butyldimethylsilyl)amide with white phosphorus yielding [dilithium 1,2-di(2-pyridyl)-1,2-bis(trialkylsilylamido)ethane] and Li_3P_7 [22]. An additional methylene group hinders the oxidative C–C coupling reaction; thus 2-pyridylethylamine only formed a zinc complex during the zincation reaction, however, the precipitation of zinc metal and a C–C coupling reaction did not occur [23].

In [di(methylzinc) 1,2-di(2-pyridyl)-1,2-bis(trialkylsilylamido)ethanes] **G** [20, 21] as well as in the corresponding ruthenium complexes [11, 12] the metal atoms show very close contacts or metal-metal bonds, respectively. In order to investigate the influence of the small Zn···Zn distance on the reactivity of these complexes, we intended to prepare 1,4-diamino-2,3-di(2-pyridyl)butanes **B** with a larger bite (N···N distance). Here we report on the synthesis of this tetradentate Lewis base 1,4-diamino-2,3-di(2-pyridyl)butane **B** (R = H) and the formation of a zinc(II) chloride complex.

Results and Discussion

Due to the failure of the above mentioned metal-mediated oxidative C–C coupling reaction a novel procedure had to be developed for the synthesis of 1,4-diamino-2,3-di(2-pyridyl)butane **B**. Therefore, *N*-(2-pyridylmethylidene)-methylamine (*N*-methyl-pyridine-2-carboxaldimine) (**1**) was used as starting material which was first reported by Busch and Bailar [24]. Bähr and Döge [25] isolated the compound and observed the formation of a crystalline solid in pure *N*-(2-pyridylmethylidene)methylamine upon standing for several months. Vasylyev *et al.* [26] recognized the formation of 1,3,5-trimethyl-2,4,6-tris(2-pyridyl)hexahydro-*s*-triazine, $(\mathbf{1})_3$, on the basis of IR, UV/Vis, Raman, and NMR spectroscopic investigations. They also pointed out that monomerization of this triazine occurs in solution and is catalyzed by acids. Even though several triazines have already been structurally characterized (*e. g.* 2,4,6-trimethyl-1,3,5-triazine [27], 2,4,6-tris(2-pyridyl)-1,3,5-triazine [28], and *N*-alkylated 2,4,6-tris(2-pyridyl)-1,3,5-triazine [29]), we now also determined the crystal structure of 1,3,5-trimethyl-2,4,6-tris(2-pyridyl)-

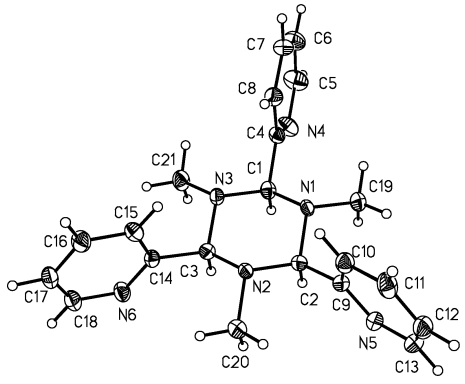
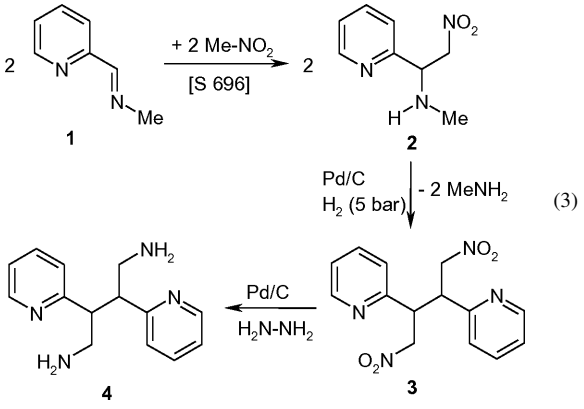


Fig. 1. Molecular structure and numbering scheme of 1,3,5-trimethyl-2,4,6-tris(2-pyridyl)hexahydro-*s*-triazine $(\mathbf{1})_3$ (displacement ellipsoids at the 40 % probability level, H atoms with arbitrary radii). Selected bond lengths (pm): N1–C1 147.5(5), N1–C2 145.8(5), N1–C19 148.2(5), N2–C2 147.1(5), N2–C3 147.5(5), N2–C20 147.0(5), N3–C1 146.3(5), N3–C3 147.5(5), N3–C21 147.0(5), C1–C4 152.2(5), C2–C9 151.0(5), C3–C14 151.3(5).

hexahydro-*s*-triazine, $(\mathbf{1})_3$. Molecular structure and numbering scheme of $(\mathbf{1})_3$ (trimeric *N*-(2-pyridylmethylidene)-methylamine **1**) are shown in Fig. 1. The central triazine ring of the C_3-symmetric molecule is found in a chair conformation with all pyridyl and methyl groups in equatorial positions which is in agreement with the proposed structure of Vasylyev *et al.* [26]. All N–C–N (av. value 109.2°) and C–N–C (av. value 110.3°) bond angles as well as C–N bond lengths (av. C–N 147.0 pm) of the inner cycle are in the expected ranges.

Nitromethane was added to freshly distilled monomeric *N*-(2-pyridylmethylidene)-methylamine (**1**) in the presence of magnesium aluminum hydroxide carbonate (Syntal® 696, Süd-Chemie AG) yielding 1-methylamino-1-(2-pyridyl)-2-nitroethane (**2**) according to Eq. 3 in a Henry-type reaction. This compound was formed nearly quantitatively as an orange oil which decomposed slowly to a dark brown waxy residue. Air-contact accelerated this decomposition reaction whereas dilution slowed this process down. Therefore, **2** was stored at −78 °C as a methanol solution.

The carbon atom which is substituted by 2-pyridyl and methylamino groups is chiral and therefore, the hydrogen atoms of the neighboring methylene moiety are diastereotopic leading to an ABX-type spectrum. The geminal $^2J(H_A,H_B)$ coupling constant shows a value of 12.4 Hz, the vicinal coupling constants are $^3J(H_A,H_X)$ = 5.2 Hz and $^3J(H_B,H_X)$ = 8.6 Hz with



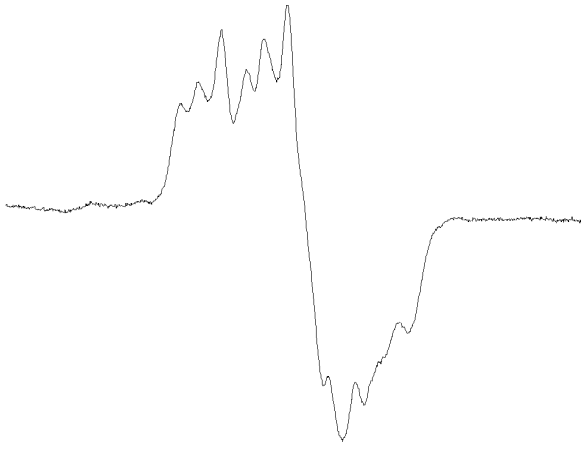
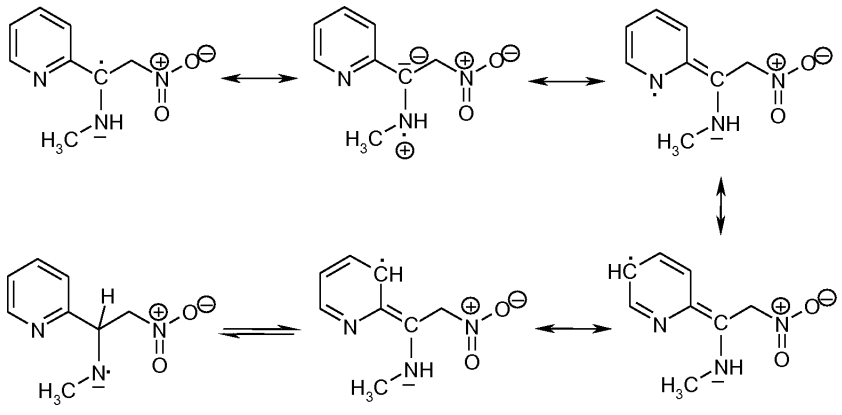


Fig. 2. EPR signal of the 1-methylamino-1-(2-pyridyl)-2-nitroethane radical generated from **2** in benzene at 25 °C (see Scheme 2).

chemical shifts of $\delta(H_A)$ = 4.26, $\delta(H_B)$ = 4.39, and $\delta(H_X)$ = 4.10.

In an EPR experiment with **2** organic radical species were detected at g = 2.0032. The EPR spectrum is shown in Fig. 2. The shape of the signal suggests that two organic radicals are present. Therefore, the simulation can only give rough clues about the hyperfine coupling constants. Best results for the major radical were obtained with a(N) = 9 G and a(H) = 4.5 G. The proposed radical is formed *via* a hydrogen abstraction from **2** and is shown in Scheme 2 with its mesomeric forms and one tautomeric isomer. The presence of this radical is in agreement with the fact that **2** slowly decomposes in solution at low temperatures. However, decomposition is significantly accelerated in the presence of air and after isolation of **2** as an oily substance.

The C–C coupling of **2** was performed with a Pd/C catalyst system in methanol and under a hydrogen



Scheme 2. Mesomeric and tautomeric forms of the 1-methylamino-1-(2-pyridyl)-2-nitroethyl radical produced by hydrogen abstraction from **2**.

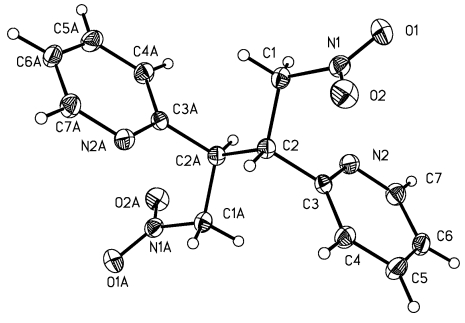


Fig. 3. Molecular structure and numbering scheme of centrosymmetric 1,4-dinitro-2,3-di(2-pyridyl)butane, *meso*-**3** (symmetry-related atoms $(-x, -y+1, -z+1)$ are marked with the letter "A"; displacement ellipsoids at the 40 % probability level, H atoms with arbitrary radii). Selected bond lengths (pm): N1–O1 122.4(3), N1–O2 122.5(3), N1–C1 149.8(3), N2–C3 134.1(3), N2–C7 134.1(3), C1–C2 153.5(3), C2–C3 150.9(3), C2–C2A 155.4(5), C3–C4 138.4(4), C4–C5 138.1(4), C5–C6 138.0(4), C6–C7 137.6(4).

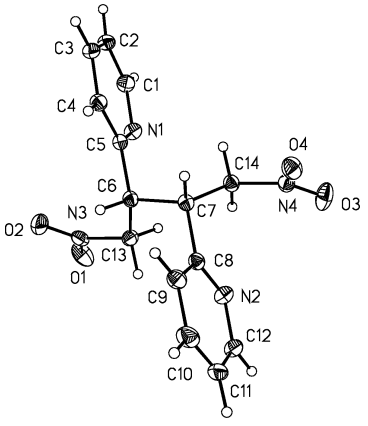


Fig. 4. Molecular structure and numbering scheme of non-centrosymmetric 1,4-dinitro-2,3-di(2-pyridyl)butane, $(R,R)/(S,S)$-**3** (displacement ellipsoids at the 40 % probability level, H atoms with arbitrary radii). Selected bond lengths (pm): N1–C1 134.2(2), N1–C5 134.0(2), N2–C8 134.0(2), N2–C12 134.8(2), N3–C13 149.4(2), N3–O1 122.2(2), N3–O2 122.0(2), N4–O3 121.5(2), N4–O4 122.4(2), C1–C2 137.8(2), C2–C3 137.8(3), C3–C4 138.1(2), C4–C5 139.2(2), C5–C6 151.7(2), C6–C7 151.7(2), C6–C13 152.2(2), C7–C8 152.5(2), C7–C14 152.8(2), C8–C9 138.5(2), C9–C10 138.1(3), C10–C11 137.3(3), C11–C12 137.5(3).

pressure of 5 bar leading to the formation of 1,4-dinitro-2,3-di(2-pyridyl)butane (**3**) in rather poor yield. The major reason for a yield of approximately 12 % might be that the nitro groups were also attacked under these reaction conditions. Nevertheless, this compound could be isolated with ease by cooling of the reaction mixture to −20 °C and therefore, the rather poor yield seems to be acceptable. The major product was *meso*-1,4-dinitro-2,3-di(2-pyridyl)butane (*meso*-**3**) whereas only traces of the (R,R)- and (S,S)-enantiomers were isolated. Therefore, the NMR data presented in the Experimental Section refer to the *meso* isomer.

Compound **3** crystallizes either as the *meso* form (*meso*-**3**) or as the (R,R)- and (S,S)-enantiomers. The *meso*-isomer exhibits crystallographic inversion symmetry and is displayed in Fig. 3. Molecular structure and numbering scheme of the (R,R)-enantiomer of **3** are shown in Fig. 4. The structural parameters of these isomers are very much alike and are discussed together.

The central C–C bond is the longest bond in the molecule due to the rather high degree of substitution and due to repulsive electrostatic forces between two carbon atoms of identical charge. The nitro groups contain N atoms in a planar environment with N–C bond lengths of 149.3(2) pm for the (R,R)-isomer and of 149.8(3) pm for the *meso* form.

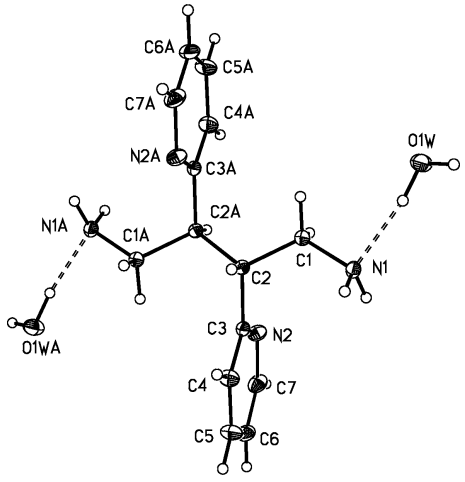


Fig. 5. Molecular structure and numbering scheme of centrosymmetric 1,4-diamino-2,3-di(2-pyridyl)butane hydrate, *meso*-**4**·H_2O (symmetry-related atoms ($-x+2$, $-y+1$, $-z+1$) are marked with the letter "A"; displacement ellipsoids at the 40 % probability level, H atoms with arbitrary radii). Selected bond lengths (pm): N1–C1 146.6(2), N2–C3 134.0(2), N2–C7 134.1(2), C1–C2 153.6(2), C2–C3 151.2(2), C2–C2A 155.6(2), C3–C4 138.5(2), C4–C5 138.5(2), C5–C6 136.8(3), C6–C7 137.6(3).

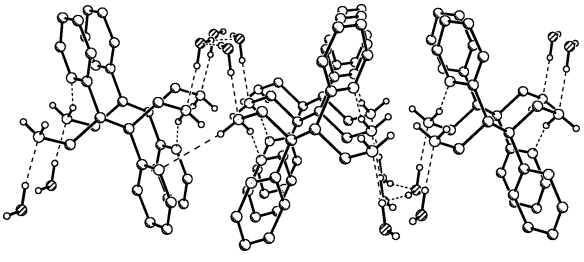
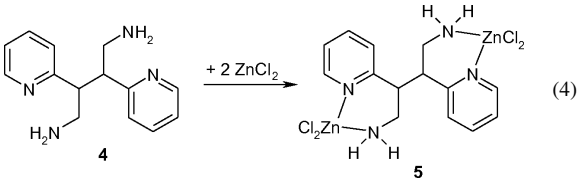


Fig. 6. Packing of *meso*-**4**·$2H_2O$ in the crystalline state showing the hydrogen bonds and part of the resulting corrugated layer structure.

The nitro functionalities of **3** were converted into amino groups with hydrazine hydrate in the presence of a Pd/C catalyst system [30]. Tetradentate *meso*-1,4-diamino-2,3-di(2-pyridyl)butane **4** was isolated from this reduction reaction with a yield of 76 %. During reduction of the volume of the reaction mixture in vacuum, **4** precipitated as a colorless microcrystalline powder. Recrystallization of **4** from an aqueous solution afforded the colorless hydrate **4**·$2H_2O$.

Molecular structure and numbering scheme of **4**·$2H_2O$ as the *meso* isomer are shown in Fig. 5. The water molecules show hydrogen bridges to the amino groups and neighboring water molecules. This bonding pattern leads to a corrugated layer structure,



(4)

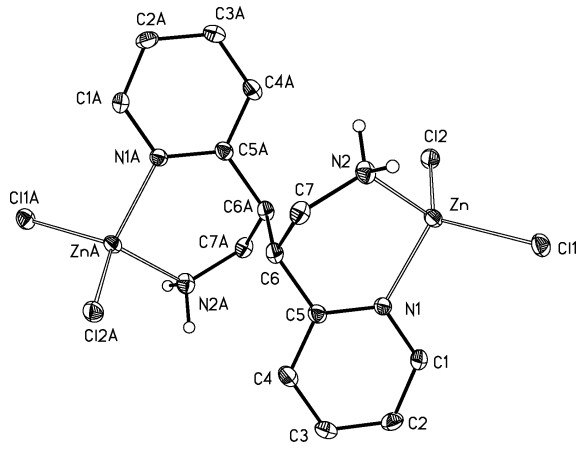


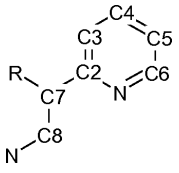
Fig. 7. Molecular structure and numbering scheme of the centrosymmetric zinc(II) chloride complex of 1,4-diamino-2,3-di(2-pyridyl)butane hydrate **5** (symmetry-related atoms ($-x+1$, $-y+1$, $-z+1$) are marked with the letter "A"; displacement ellipsoids at the 40 % probability level, only the amino hydrogen atoms are shown). Selected bond lengths (pm): Zn–N1 205.4(3), Zn–N2 204.9(4), Zn–Cl1 222.3(1), Zn–Cl2 223.9(1), N1–C1 134.7(5), N1–C5 135.0(5), N2–C7 148.5(5), C1–C2 137.5(5), C2–C3 137.3(6), C3–C4 137.3(6), C4–C5 138.6(5), C5–C6 152.1(5), C6–C6A 153.0(7), C6–C7 153.6(5).

as shown in Fig. 6. The rather large O···O and O···N contacts suggest that only weak hydrogen bridges are formed. This fact is in agreement with the observation that the anhydrous amine could be obtained at 10^{-2} mm Hg and 30 °C. The N–C bond lengths of these amino groups exhibit values of 146.6(2) pm.

In order to compare the coordination behavior of **4** with that of related ligands in already known complexes, *meso*-1,4-diamino-2,3-di(2-pyridyl)butane (**4**) was added to zinc(II) chloride in a THF solution. Dinuclear [*meso*-1,4-diamino-2,3-di(2-pyridyl)butane bis(dichlorozinc)] (**5**) formed quantitatively as a colorless crystalline solid, as shown in Eq. 4. In this complex the zinc atoms are in distorted tetrahedral environments.

In contrast to our findings, Uhlig and Maaser [31] suggested a polymeric structure of [2-(aminoethyl)pyridine dichlorozinc] where the two nitrogen bases of the ligand are bound to different zinc atoms. How-

Table 1. Comparison of selected NMR parameters (chemical shifts in ppm). The numbering scheme is given below and differs from the crystallographic numbering used in the X-ray structure determinations.



	2	**3**	**4**	**5**
^{1}H NMR:				
δ(H7)	4.09	4.12	3.19	3.55
δ(H8a)	4.26	4.66	2.31	2.74
δ(H8b)	4.39	5.04	2.65	2.99
δ(NH_2)	–	–	1.98	4.10
^{13}C{^{1}H} NMR:				
δ(C7)	63.1	46.5	44.6	42.8
δ(C8)	78.8	76.4	52.5	47.9

ever, later investigations on closely related substituted amines showed that these Lewis bases act as chelating ligands [32, 33]. A crystal structure determination by X-ray diffraction of [6-{2-(dimethylamino)-phenyl}-2,2′-bipyridine zinc dichloride] showed a penta-coordinate zinc atom with Zn–N bond lengths of 214.2 and 230.8 pm to the pyridyl and the amino groups, respectively, and Zn–Cl distances of 224.5 and 230.7 pm [34].

Molecular structure and numbering scheme of the dinuclear complex **5** are displayed in Fig. 7. The coordination of the zinc cation at the amino group (substitution of water by zinc(II) chloride) leads to a slight elongation of the N1–C1 bond. The Zn–N bonds to the amino and to the pyridyl groups are similar within standard deviations. Due to steric hindrance the Zn–Cl1 bond is slightly shorter than the Zn–Cl2 bond. However, both values lie well within the characteristic region [35]. The coordination sphere of the zinc atoms in this complex is rather similar to that in (bpy)$ZnCl_2$ (bpy = 2,2′-bipyridine) [36] and therefore, the tetradentate ligand can be considered as a strong chelate base. In complexes of the type $(L)_2ZnX_2$ (L = Lewis base with a nitrogen donor, X = any mono anion) with a tetra-coordinate zinc atom, a linear correlation between the X–Zn–X angle and the average Zn–N distance was found [37, 38]. Thus, strong nitrogen donors with short Zn–N bond lengths lead to small X–Zn–X angles and *vice versa*. In (1-amino-3-dimethylaminopropane)zinc dichloride an average Zn–N distance of 203.6 pm and a Cl–Zn–Cl angle of 112.55(3)° were observed [39]. In (tmeda)$ZnCl_2$ larger Zn–N bonds of 209.2 pm allow a larger Cl–Zn–Cl bond angle of 119.00(2)° [40, 41].

Selected NMR data of **2** to **5** are summarized in Table 1. The ^{1}H as well as the ^{13}C{^{1}H} NMR parameters of the pyridyl group show only a very small dependency of the substitution pattern at the alkyl group. Therefore, only the values of the C7–C8 units are compared in Table 1. The nitro group leads to deshielded methylene moieties in **2** and **3** whereas amino substitution leads to chemical shifts of approximately 50 ppm for C8. The hydrogen atoms at C8 are diastereotopic due to the chirality of neighboring C7. A highfield shift of approximately 2 ppm is observed when the nitro group is reduced to the amino functionality.

Conclusion

Oxidative C–C coupling of 2-pyridylmethylamines can be performed quantitatively with organozinc or tin(II) compounds with precipitation of metal. Another access route to 1,2-dipyridyl-1,2-diaminoethane is the reductive coupling of 2-pyridylmethylidene amine. For 2,3-dipyridyl-1,4-diaminobutane no comparable reaction routes had been available.

The addition of nitromethane to *N*-methyl-(2-pyridyl)methylimine (*N*-methyl-2-pyridylmethylideneamine) gives 1-methylamino-1-(2-pyridyl)-2-nitroethane (**2**) with a good yield. In a hydrogen atmosphere methylamine can be eliminated, and C–C coupling is achieved with a rather poor yield due to side-reactions, leading to the formation of 1,4-dinitro-2,3-di(2-pyridyl)butane (**3**). The conversion of the nitro functionalities into amino groups is achieved with hydrazine hydrate giving 1,4-diamino-2,3-di(2-pyridyl)butane (**4**). Due to the presence of two chiral carbon atoms in 2- and 3-position in the backbone of **3** and **4** the formation of diastereomers and enantiomers is observed.

1,2-Dipyridyl-1,2-diaminoethane easily isomerizes during metalation with dialkylzinc. Therefore, zincation of *meso*- and (*R*,*R*)/(*S*,*S*)-1,2-dipyridyl-1,2-diaminoethane yields bis(alkylzinc) (*R*,*R*)/(*S*,*S*)-1,2-dipyridyl-1,2-diamidoethane regardless of the employed isomer. First reactivity studies of 1,4-diamino-2,3-di(2-pyridyl)butane (**4**) show that isomerization occurs far less readily. The zinc(II) chloride adduct, [*meso*-1,4-diamino-2,3-di(2-pyridyl)butane bis(dichlorozinc)] (**5**), is formed quantitatively from *meso*-**3**. Due to the longer butane chain, ligand **4** shows an enhanced flexibility compared to 1,2-dipyrid-

yl-1,2-diaminoethane with its short backbone. The coordination behavior of **4** will be explored in more detail in the future.

Experimental Section

General remarks

All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. The solvents were dried according to common procedures and distilled under argon. Deuterated solvents were dried over sodium, degassed, and saturated with argon. The ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on a Bruker AC 400 MHz spectrometer. Mass spectra were obtained on a Finnigan MAT SSQ 710 system, and IR measurements were carried out using a Perkin-Elmer System 2000 FTIR. The IR spectra were taken as Nujol mulls between KBr windows. Melting and decomposition points were measured with a Reichert-Jung apparatus type 302102 and are uncorrected. Süd-Chemie AG (Moosburg, Germany) put the hydrotalcite Syntal® 696 (aluminum magnesium hydroxy carbonate, 20.8 % Al_2O_3, 33.8 % MgO) to our disposal. *N*-(2-Pyridylmethylidene)-methylamine (**1**) was prepared according to literature procedures [24 – 26].

*Synthesis of 1-methylamino-1-(2-pyridyl)-2-nitroethane (**2**)*

N-Methyl-(2-pyridyl)methylimine (32.0 g, 266 mmol) and 6 g of Syntal® 696 were suspended in 208 mL of nitromethane and stirred at 15 °C for 5 h. Then the catalyst was removed by filtration. Under reduced pressure, all volatile materials were removed, and 35.5 g of an orange oil (200 mmol, 74 %) remained. – ^{1}H NMR ([D$_6$]benzene): δ = 8.30 (d, ^3J(H^6,H^5) = 4.4 Hz, 1H, Pyr^6), 7.01 (ddd, ^3J(H^4,H^{3,5}) = 7.9 Hz, ^4J(H^4,H^6) = 1.6 Hz, 1H, Pyr^4), 6.76 (d, ^3J(H^3,H^4) = 7.9 Hz, 1H, Pyr^3), 6.59 (ddd, ^3J(H^5,H^4) = 7.6 Hz, ^3J(H^5,H^6) = 4.4 Hz, ^4J(H^5,H^3) = 0.8 Hz, 1H, Pyr^5), 4.39 (m, ^2J(H^{8b},H^{8a}) = 12.4 Hz, ^3J(H^{8b},H^7) = 8.6 Hz, 1H, H^{8b}), 4.26 (m, ^2J(H^{8a},H^{8b}) = 12.4 Hz, ^3J(H^{8a},H^7) = 5.2 Hz, 1H, H^{8a}), 4.09 (m, ^3J(H^7,H^{8a}) = 5.2 Hz, ^3J(H^7,H^{8b}) = 8.6 Hz, 1H, H^7), 1.96 (s, 3H, H^9); 1.72 br-s, (1H, H^{10}). – ^{13}C NMR ([D$_6$]benzene): δ = 158.4 (Pyr^2), 149.8 (Pyr^6), 136.2 (Pyr^4), 122.7 (Pyr^{3,5}), 78.8 (C^8), 63.1 (C^7), 33.6 (C^9).

*Synthesis of 1,4-dinitro-2,3-di(2-pyridyl)butane (**3**)*

1-Methylamino-1-(2-pyridyl)-2-nitroethane (**2**) (6 g, 33.1 mmol) was stirred in an autoclave with 100 mg palladium catalyst in 45 mL methanol at 5 bar hydrogen pressure at −5 °C for 24 h. Thereafter, the nearly insoluble product **3** was separated without warming of the reaction mixture and washed twice with cold methanol. Separation from the catalyst was performed *via* extraction of **3** with dichloromethane. After removal of all volatile materials under vacuum, 600 mg of a white powder (2 mmol, 12 %) remained. M. p.: 182 °C (dec.). – ^{1}H NMR ([D$_6$]DMSO): δ = 8.52 (d, ^3J(H^6,H^5) = 4.8 Hz, ^4J(H^6,H^4) = 1.7 Hz, 1H, Pyr^6), 7.74 (ddd, ^3J(H^4,H^{3,5}) = 7.6 Hz, ^4J(H^4,H^6) = 1.7 Hz, 1H, Pyr^4), 7.29 (m, 2H, Pyr$^{3/5}$), 5.04 (m, 1H, H^{8a}), 4.66 (pdd, 1H, H^{8b},), 4.12 (m, 1H, H^7). – ^{13}C NMR ([D$_6$]DMSO): δ = 156.6 (Pyr^2), 149.3 (Pyr^6), 137.0 (Pyr^4), 124.4 (Pyr^3), 122.9 (Pyr^5), 76.4 (C^8), 46.5 (C^7). – IR (KBr, cm^{-1}): ν = 3441 m/br, 3090 w, 3063 w, 3017 m, 2910 w, 1592 s, 1570 m, 1538 vs, 1474 s, 1440 m, 1425 s, 1380 s, 1337 w, 1295 m, 1256 w, 1209 m, 1148 w, 1092 w, 1051 m, 1001 m, 977 w, 913 w, 810 s, 782 m, 756 s, 629 vw, 619 m, 592 m, 539 m, 483 w, 407 w. – MS (EI): *m*/*z* (%) = 303 (19) [M+H]$^+$, 256 (100) [M–NO$_2$,–H]$^+$, 209 (73) [M–2NO$_2$,–2H]$^+$, 194 (23) [209–CH$_3$]$^+$. – $C_{14}H_{14}N_4O_4$ (302.29): calcd. C 55.63, H 4.67, N 18.53; found C 55.48, H 4.62, N 18.61.

*Synthesis of 1,4-diamino-2,3-di(2-pyridyl)butane (**4**)*

1,4-Dinitro-2,3-di(2-pyridyl)butane (**3**) (351 mg, 1,45 mmol) and 300 mg Pd/C catalyst were suspended in 70 mL of anhydrous ethanol and heated under reflux. Hydrazine-hydrate (8 mL) was added dropwise; thereafter the solution was boiled for additional 10 h. Then the catalyst was removed. The solution was concentrated till a precipitate formed. Storage at −20 °C led to the precipitation of 214 mg of **4** (0.88 mmol, 76 %). M. p.: 106 °C. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.58 (dd, ^3J(H^6,H^5) = 4.9 Hz, ^4J(H^6,H^4) = 1.2 Hz, 1H, Pyr^6), 7.71 (ddd, ^3J(H^4,H^{3,5}) = 7.4 Hz, ^4J(H^4,H^6) = 1.2 Hz, 1H, Pyr^4), 7.29 (d, ^3J(H^3,H^4) = 7.6 Hz, 1H, Pyr^3), 7.23 (ddd, ^3J(H^5,H^4) = 7.4 Hz, ^3J(H^5,H^6) = 4.9 Hz, ^4J(H^5,H^3) = 1.2 Hz, 1H, Pyr^5), 3.19 (m, 1H, H^7), 2.65 (m, 1H, H^{8a}), 2.31 (m, 1H, H^{8b}), 1.98 (s, 2H, H^9). – ^{13}C NMR ([D$_6$]DMSO): δ = 149.3 (Pyr^6), 136.0 (Pyr^4), 124.6 (Pyr^3), 121.5 (Pyr^5), 162.2 (Pyr^2), 52.5 (C^7), 44.6 (C^8). – IR (KBr, cm^{-1}): ν = 3448 vw, 3344 s, 3271 s, 3191 w, 3081 m, 3057 m, 3012 s, 2985 w, 2933 vs, 2919 vs, 2860 s, 2296 vw, 1970 w, 1590 vs, 1567 vs, 1474 vs, 1434 vs, 1356 m, 1334 w, 1292 m, 1250 w, 1227 m, 1146 s, 1085 s, 1053 m, 997 vs, 984 vs, 920 vw, 888 vs, 799 vs, 774 m, 757 m, 634 m, 613 m, 548 w, 487 w, 440 w, 407 m. – MS (EI): *m*/*z* (%) = 243 (7) [M]$^+$, 183 (100) [M–2·CH$_2$NH$_2$]$^+$, 122 (51) [M–PyrC$_2$H$_3$NH$_2$]$^+$, 121 (48) [122–H]$^+$, 105 (22) [121–NH$_2$]$^+$, 30 (9) [CH$_2$NH$_2$]$^+$. – $C_{14}H_{18}N_4$ (242,33): calcd. C 69.39, H 7.49, N 23.12; found C 69.16, H 6.96, N 22.90.

*Synthesis of [meso-1,4-diamino-2,3-di(2-pyridyl)butane-bis(dichlorozinc)] (**5**)*

72 mg of 1,4-diamino-2,3-di(2-pyridyl)butane (**4**) (0.298 mmol) was dissolved in 2 mL of THF and dropped into a solution of 82 mg (0.60 mmol) of $ZnCl_2$ in 5 mL of THF. A colorless precipitate formed and was washed twice

Table 2. Crystal data and refinement details for the crystal structure determinations of $(\mathbf{1})_3$, *meso*-**3**, *(R,R)/(S,S)*-**3**, *meso*-**4**, and **5**.

Compound	$(\mathbf{1})_3$	*meso*-**3**	*(R,R)/(S,S)*-**3**	*meso*-**4**	**5**
Formula	$C_{21}H_{24}N_6$	$C_{14}H_{14}N_4O_4$	$C_{14}H_{14}N_4O_4$	$C_{14}H_{18}N_4 * 2H_2O$	$C_{14}H_{18}Cl_4N4Zn_2$
M_r, g mol^{-1}	360.46	302.29	302.29	278.36	514.86
T, °C	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, pm	1029.18(15)	692.76(8)	948.11(7)	961.60(19)	641.74(6)
b, pm	1036.38(15)	555.43(7)	1059.70(5)	1478.4(3)	913.20(9)
c, pm	1121.31(15)	1817.82(12)	1460.23(9)	520.63(10)	934.39(9)
α, deg	93.352(7)	90	90	90	66.501(5)
β, deg	111.797(7)	100.519(7)	104.094(3)	96.74(3)	78.692(7)
γ, deg	117.066(6)	90	90	90	71.013(5)
V, Å^3	950.7(2)	687.71(13)	1422.95(15)	735.0(3)	473.46(8)
Z	2	2	4	2	1
D_x, g cm^{-3}	1.259	1.460	1.411	1.258	1.806
μ(MoK_α), cm^{-1}	0.79	1.1	1.06	0.87	31.01
Measured data	6681	4245	9784	5140	3316
Unique data/R_{int}	4209/0.1057	1563/0.0595	3250/0.0417	1690/0.0454	2139/0.0341
Data with $I \geq 2\sigma(I)$	1501	942	2325	1228	1641
R_1 [$I \geq 2\sigma(I)$][a]	0.0837	0.0606	0.0476	0.0422	0.0412
wR_2 (all data, on F^2)[a]	0.2043	0.1547	0.1360	0.1098	0.1015
Weighting scheme a/b[a]	0.0633/0.0000	0.0643/0.3072	0.0678/0.3257	0.0512/0.1399	0.0435/0.4300
GoF (S)[b]	0.976	1.029	1.031	1.019	1.032
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.28/−0.25	0.21/−0.22	0.20/−0.30	0.22/−0.23	0.64/−0.83
CCDC no.	720858	720859	720860	720861	720862

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w({F_o}^2 - {F_c}^2)^2/\Sigma w({F_o}^2)^2]^{1/2}$, $w = [\sigma^2({F_o}^2) + (aP)^2 + bP]^{-1}$, where $P = (\mathrm{Max}({F_o}^2, 0) + 2{F_c}^2)/3$; [b] GoF = $[\Sigma w({F_o}^2 - {F_c}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

with THF. Yield: 150 mg (291 μmol, 98 %). Dec. above 280 °C without melting. – ^{1}H NMR ([D$_6$]DMSO): δ = 8.47 (dd, ^3J(H^6,H^5) = 5.1 Hz, ^4J(H^6,H^4) = 1.5 Hz, 1H, Pyr^6), 7.80 (ddd, ^3J(H^4,H^{3,5}) = 7.7 Hz, ^4J(H^4,H^6) = 1.5 Hz, 1H, Pyr^4), 7.34 (ddd, ^3J(H^5,H^4) = 7.62 Hz, ^3J(H^5,H^6) = 5.1 Hz, ^4J(H^5,H^3) = 1.8 Hz, 1H, Pyr^5), 7.23 (d, ^3J(H^3,H^4) = 7.8 Hz, 1H, Pyr^3), 3.55 (m, 1H, H^7), 2.99 (m, 1H, H^{8a}), 2.74 (m, 1H, H^{8b}), 4.1 (s, 1H, H^9). – ^{13}C NMR ([D$_6$]DMSO): δ = 148.5 (Pyr^6), 138.6 (Pyr^4), 122.8 (Pyr^5), 124.9 (Pyr^3), 161.2 (Pyr^2), 42.8 (C^7), 47.9 (C^8). – IR (KBr, cm^{-1}): ν = 3450 m, 3314 vs, 3258 vs, 3144 w, 3062 vw, 3032 vw, 2930 s, 2887 m, 1609 vs, 1586 vs, 1571 vs, 1482 vs, 1457 vw, 1442 vs, 1386 m, 1359 w, 1323 s, 1288 m, 1267 m, 1243 w, 1197 w, 1160 m, 1124 vs, 1103 m, 1064 m, 1049 m, 1030 m, 958 s, 911 w, 789 s, 772 s, 669 m, 648 s, 578 w, 561 s, 523 m, 429 vw, 418 w. – MS (EI): *m/z* (%) = 243 (6) [L]$^+$, 195 (100) [L–CH$_2$NH$_2$,NH$_4$]$^+$, 183 (81) [L–2·CH$_2$NH$_2$]$^+$, 121 (49) [L–PyrC$_2$H$_3$NH$_2$,H]$^+$, 106 (29) [121–NH$_2$)$^+$. – $C_{14}H_{18}N_4Cl_4Zn_2$ (514.94): calcd. C 32.65, H 3.52, N 10.88; found C 32.70, H 3.55, N 9.97.

Crystal structure determinations

The intensity data for the compounds 1,3,5-trimethyl-2,4,6-tris(2-pyridyl)hexahydro-*s*-triazine, $(\mathbf{1})_3$, *meso*-**3**, (*R*,*R*)- and (*S*,*S*)-**3**, **4**, and **5** were collected on a Nonius KappaCCD diffractometer using graphite-monochromatized MoK_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption [42, 43]. The structures were solved by Direct Methods (SHELXS [44]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [45]) (Table 2). For the amino group at N2 of **5**, and the whole compound of **4**, the hydrogen atoms were located in difference Fourier syntheses and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed displacement parameters. All non-hydrogen atoms were refined anisotropically [45]. Structure representations: XP (Siemens Analytical X-ray Instruments, Inc.).

CCDC 720858 – 720862 (see Table 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft (DFG, Bonn-Bad Godesberg, Germany) and the Fonds der Chemischen Industrie (Frankfurt/Main, Germany). We thank Süd-Chemie AG (Moosburg, Germany) for putting the hydrotalcite Syntal® 696 (aluminum magnesium hydroxy carbonate, 20.8 % Al_2O_3, 33.8 % MgO) to our disposal.

[1] F. Vögtle, E. Goldschmitt, *Angew. Chem*. **1973**, *85*, 824 – 826; *Angew. Chem., Int. Ed. Engl*. **1973**, *12*, 765 – 767.
[2] F. Vögtle, E. Goldschmitt, *Chem. Ber*. **1976**, *109*, 1 – 40.
[3] P. J. Campos, J. Arranz, M. A. Rodríguez, *Tetrahedron* **2000**, *56*, 7285 – 7289.
[4] B. Baruah, D. Prajapati, J. S. Sandhu, *Tetrahedron Lett*. **1995**, *36*, 6747 – 6750.
[5] A. Alexakis, I. Aujard. P. Mangeney, *Synlett* **1998**, 873 – 874.
[6] A. Alexakis, I. Aujard. P. Mangeney, *Synlett* **1998**, 875 – 876.
[7] P. Mangeney, T. Tejero, A. Alexakis, F. Grosjean, J. Normant, *Synthesis* **1988**, 255 – 257.
[8] G. Alvaro, D. Savoia, M. R. Valentinetti, *Tetrahedron* **1996**, *52*, 12571 – 12586.
[9] R. J. Baker, C. Jones, M. Kloth, D. P. Mills, *New J. Chem*. **2004**, *28*, 207 – 213.
[10] R. Annunziata, M. Benaglia, M. Caporale, L. Raimondi, *Tetrahedron* **2002**, *13*, 2727 – 2734.
[11] L. H. Polm, G. van Koten, C. J. Elsevier, K. Vrieze, B. F. K. van Santen, C. H. Stam, *J. Organomet. Chem*. **1986**, *304*, 353 – 370.
[12] L. H. Polm, C. J. Elsevier, G. van Koten, J. M. Ernsting, D. J. Stufkens, K. Vrieze, R. R. Andréa, C. H. Stam, *Organometallics* **1987**, *6*, 1096 – 1104.
[13] G. van Koten, J. T. B. H. Jastrzebski, K. Vrieze, *J. Organomet. Chem*. **1983**, *250*, 49 – 61.
[14] A. L. Spek, J. T. B. H. Jastrzebski, G. van Koten, *Acta Cryst*. **1987**, *C43*, 2006 – 2007.
[15] J. T. B. H. Jastrzebski, J. M. Klerks, G. van Koten, K. Vrieze, *J. Organomet. Chem*. **1981**, *210*, C49 – C53.
[16] E. Wissing, S. van der Linden, E. Rijnberg, J. Boersma, W. J. J. Smeets, A. L. Spek, G. van Koten, *Organometallics* **1994**, *13*, 2602 – 2608.
[17] E. Wissing, E. Rijnberg, P. A. van der Schaaf, K. van Gorp, J. Boersma, G. van Koten, *Organometallics* **1994**, *13*, 2609 – 2615.
[18] M. Westerhausen, T. Bollwein, P. Mayer, H. Piotrowski, A. Pfitzner, *Z. Anorg. Allg. Chem*. **2002**, *628*, 1425 – 1432.
[19] M. Westerhausen, T. Bollwein, N. Makropoulos, T. M. Rotter, T. Habereder, M. Suter, H. Nöth, *Eur. J. Inorg. Chem*. **2001**, 851 – 857.
[20] M. Westerhausen, T. Bollwein, N. Makropoulos, S. Schneiderbauer, M. Suter, H. Nöth, P. Mayer, H. Piotrowski, K. Polborn, A. Pfitzner, *Eur. J. Inorg. Chem*. **2002**, 389 – 404.
[21] M. Westerhausen, T. Bollwein, K. Karaghiosoff, S. Schneiderbauer, M. Vogt, H. Nöth, *Organometallics* **2002**, *21*, 906 – 911.
[22] M. Westerhausen, A. N. Kneifel, P. Mayer, *Z. Anorg. Allg. Chem*. **2006**, *632*, 634 – 638.
[23] M. Westerhausen, A. N. Kneifel, H. Nöth, *Z. Anorg. Allg. Chem*. **2006**, *632*, 2363 – 2366.
[24] D. H. Busch, J. C. Bailar, *J. Am. Chem. Soc*. **1956**, *78*, 1137 – 1142.
[25] G. Bähr, H. Döge, *Z. Anorg. Allg. Chem*. **1957**, *292*, 119 – 138.
[26] A. V. Vasylyev, L. W. Castle, D. P. Strommen, *Vibr. Spectrosc*. **1999**, *20*, 173 – 177.
[27] E. W. Lund, *Acta Chem. Scand*. **1951**, *5*, 678 – 680.
[28] M. L. Larter, M. Phillips, F. Ortega, G. Aguirre, R. Somanathan, P. J. Walsh, *Tetrahedron Lett*. **1998**, 4785 – 4788.
[29] D. A. Durham, F. A. Hart, D. Shaw, *J. Inorg. Nucl. Chem*. **1967**, *29*, 509 – 516.
[30] For a review see: A. Furst, R. C. Berlo, S. Hooton, *Chem. Rev*. **1965**, *65*, 51 – 68.
[31] E. Uhlig, M. Maaser, *Z. Anorg. Allg. Chem*. **1963**, *322*, 25 – 33.
[32] D. P. Madden, S. M. Nelson, *J. Chem. Soc. A* **1968**, 2342 – 2348.
[33] E. Uhlig, B. Borek, *Z. Anorg. Allg. Chem*. **1976**, *425*, 217 – 226.
[34] X.-m. Liu, X.-y. Mu, H. Xia, L. Ye, W. Gao, H.-y. Wang, Y. Mu, *Eur. J. Inorg. Chem*. **2006**, 4317 – 4323.
[35] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans*. **1989**, S1 – S83.
[36] M. A. Khan, D. G. Tuck, *Acta Cryst*. **1984**, *C40*, 60 – 62.
[37] M. Westerhausen, M. Wieneke, W. Schwarz, *J. Organomet. Chem*. **1996**, *522*, 137 – 146.
[38] M. Westerhausen, T. Bollwein, K. Polborn, *Z. Naturforsch*. **2000**, *55b*, 51 – 59.
[39] J.-L. Huang, Y.-L. Feng, *Acta Cryst*. **2007**, *E63*, m1395.
[40] S. Hooton, M. F. C. Ladd, *J. Cryst. Mol. Struct*. **1973**, *3*, 95 – 102.
[41] D.-M. Chen, X.-J. Ma, B. Tu, W.-J. Feng, Z.-M. Jin, *Acta Cryst*. **2006**, *E62*, m3174–m3175.
[42] COLLECT, Nonius KappaCCD Software, Nonius BV, Delft (The Netherlands) **1998**.
[43] Z. Otwinowski, W. Minor in *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A (Eds.: C. W. Carter Jr, R. M. Sweet), Academic Press, New York, **1997**, pp. 307 – 326.
[44] G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467 – 473.
[45] G. M. Sheldrick, SHELXL-97 (release 97-2), Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**; see also: G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112 – 122.