Alkylzinc Complexes with Achiral and Chiral Monoanionic *N,N,O* Heteroscorpionate Ligands

Ina Hegelmann,[a] Alexander Beck,[a] Christian Eichhorn,[b] Bernhard Weibert,[a] and Nicolai Burzlaff*[a]

Keywords: Scorpionate ligands / Zinc / Bioinorganic chemistry / Tripodal ligands / N ligands

The synthesis of the new chiral ligand (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid (bpaH^{tBu2,Me2}) (**4**) has been achieved. Two different synthetic routes to its precursor 3,5-di-*tert*-butyl-1-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole (bpm^{tBu2,Me2}) (**3**) are reported. Deprotonation at the methylene group, followed by reaction with carbon dioxide, yielded a racemic mixture of **4**. The chemical behaviour of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (bd*t*bpzaH) (**2**) and the new chiral *N,N,O* scorpionate ligand **4** involving their coordination to zinc ions was studied. [Zn(bpa^{tBu2,Me2})Cl] (**5**) was formed from a mixture of $ZnCl_2$, **4** and base. Reaction of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (bd*t*bpzaH) (**2**) with $Zn(CH_3)_2$ or $Zn(CH_2CH_3)_2$ gave the alkylzinc complexes [Zn(bd*t*bpza)(CH_3)] (**6**) and [Zn(bd*t*bpza)(CH_2CH_3)] (**7**). [Zn(bpa^{tBu2,Me2})(CH_3)] (**8**) was obtained from a synthesis analogous to that of **6** with **4**. The further reactions of **6** and **8** with acetic acid resulted in the acetato complexes [Zn(OAc)(bd*t*bpza)] (**9**) and [Zn(OAc)(bpa^{tBu2,Me2})] (**10**). The chiral methyl complex **8** may serve as a precursor for structural model complexes of the active sites of zinc enzymes, such as thermolysin or carboxypeptidase A. [Zn(bpa^{tBu2,Me2})$_2$] (**11**) was formed from a side reaction. Crystal structures of **4**, **5**, **8** and **11** were obtained; **5** crystallised as the dimer [Zn(bpa^{tBu2,Me2})Cl]$_2$; **11** presents an unusual zinc binding geometry.

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Introduction

Zinc complexes with *N,N,O* ligands can serve as models for the active site of zinc-containing enzymes that bind the metal ion with two histidine groups and one aspartate or glutamate group. Examples are carboxypeptidase A, thermolysin (Figure 1) and other proteases.[1–5]

There are only a few examples of *N,N,O* tripod ligands that mimic this motif. Carrano et al. used the scorpionate ligand (3-*tert*-butyl-2-hydroxy-5-methylphenyl)bis(3,5-dimethylpyrazol-1-yl)methane to generate model complexes of zinc-containing enzymes.[6] However, instead of a carboxylate *O*-donor, this ligand contained a phenolate *O*-donor. By insertion of formaldehyde or carbon dioxide into a B–H bond of zinc bis(pyrazol-1-yl)hydroborate complexes, Parkin et al. also formed *N,N,O* model complexes.[7] Recently, we reported on the synthesis of structural models for this class of enzymes by using bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid.[8]

Since enzymes are chiral compounds there has been a major effort in bioinorganic chemistry to supply chiral models for the active sites of metalloenzymes. Alsfasser et al.[9] and Vahrenkamp et al.[10] achieved this by including amino acids in the ligand systems. Modification of hydrotris(pyrazol-1-yl)borate (Tp) ligands by chiral pyrazoles de-

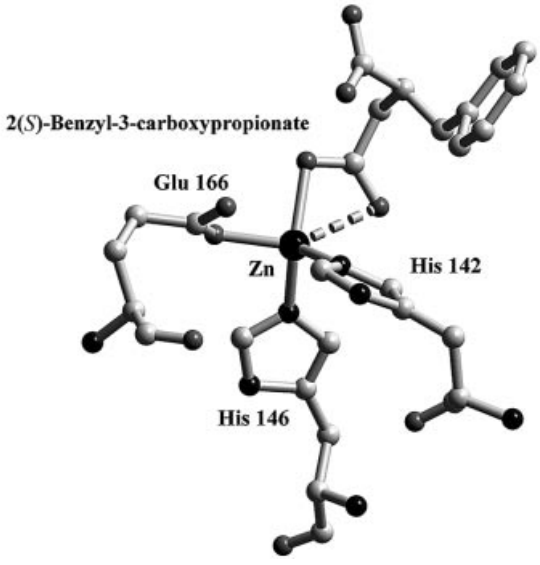


Figure 1. Active site of thermolysin with inhibitor (2*S*)-2-benzyl-3-carboxypropionic acid bound to a zinc ion (PDB-Code: 1HYT)[5]

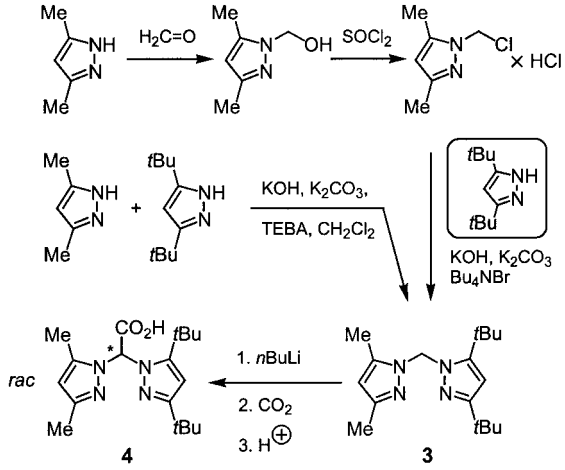
[a] Fachbereich Chemie der Universität Konstanz,
Universitätsstraße 10, Fach M728, 78457 Konstanz, Germany
Fax: (internat.) + 49-(0)7531/88-3136
E-mail: nicolai@chemie.uni-konstanz.de
[b] Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, 97074 Würzburg, Germany

rived from the chiral pool is another way to form chiral *N*,*N*,*N* tripod ligands. This was the method used by Tolman et al.[11]

In recent years some of these zinc model complexes have been tested as catalysts for CO_2 activation.[12] Major progress has been made by using Zn^{II}-based catalysts for the copolymerisation of carbon dioxide and epoxides with the focus being on the tacticity of the polycarbonates.[13,14]

Results and Discussion

Based on the ligand synthesis of bdmpza published by Otero et al.,[15] we recently developed a simple synthesis for the sterically hindered bd*t*bpzaH (**2**) suitable for use in forming the model complexes [Zn(bd*t*bpza)Cl].[8] This route was also applied in the synthesis of a racemic mixture of a new chiral *N*,*N*,*O* scorpionate ligand. The unsymmetrical 3,5-di-*tert*-butyl-1-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole (bpm^{tBu2,Me2}) (**3**) served as the starting material.[16] It was obtained by a phase-transfer-catalysed reaction of 1-chloromethyl-3,5-dimethylpyrazole hydrochloride with 3,5-di-*tert*-butylpyrazole under basic conditions (Scheme 1). However, the one-step phase-transfer-catalysed reaction of 3,5-dimethylpyrazole with 3,5-di-*tert*-butylpyrazole, dichloromethane and base was more convenient (Scheme 1).



Scheme 1

After separation by column chromatography on silica, **3** was isolated in a yield of up to 17% from the reaction mixture of the three possible products. Since the other two products bis(3,5-dimethylpyrazol-1-yl)methane and especially bis(3,5-di-*tert*-butylpyrazol-1-yl)methane (**1**) can also be isolated in pure form and used for further syntheses, the second synthetic route is currently preferred. Two sets of signals are detected for the two different pyrazolyl rings in the ^1H and ^{13}C NMR spectra. Two medium-intensive IR bands at 1559 and 1541 cm^{-1} are also found for these two pyrazolyl rings.

Deprotonation of a methylene group in **3** followed by reaction with carbon dioxide and acidic workup yielded a racemic mixture of (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid (bpaH^{tBu2,Me2}) (**4**) (Scheme 1). As in **3** two sets of signals are found in the IR, ^1H and ^{13}C NMR spectra. A strong IR band at 1758 cm^{-1} and a ^1H NMR signal at $\delta = 11.09$ ppm are an indication of the carboxylate group. Crystals of **4** suitable for X-ray structure determination were obtained by crystallisation from acetone (Figure 2). Bond lengths and bond angles in **4** (Table 1) are in good agreement with those reported earlier for bd*t*bpzaH (**2**).[8]

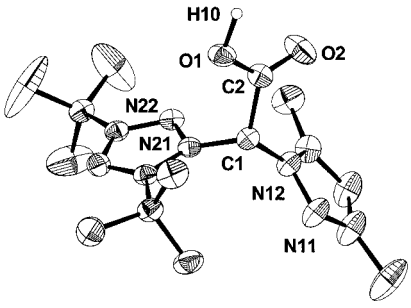


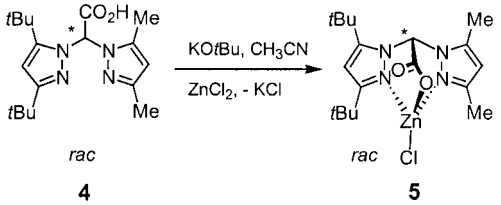
Figure 2. Molecular structure of bpaH^{tBu2,Me2} (**4**); thermal ellipsoids are drawn at the 50% probability level

Table 1. Selected bond lengths and angles of **4**

Distance [Å]	**4**	Angle [°]	**4**
C(1)−C(2)	1.540(3)	O(1)−C(2)−O(2)	125.2(2)
C(2)−O(1)	1.318(3)	C(2)−C(1)−N(12)	113.17(17)
C(2)−O(2)	1.205(3)	C(2)−C(1)−N(22)	111.26(17)
C(1)−N(12)	1.463(3)	N(12)−C(1)−N(22)	113.88(17)
C(1)−N(22)	1.454(3)		

The proton of the carboxylate group was located. It forms an intermolecular hydrogen bond to a pyrazole nitrogen atom of another molecule [*d*(H10−N11) = 1.576(3) Å].

Reaction of **4** with base and water-free $ZnCl_2$ yielded [Zn(bpa^{tBu2,Me2})Cl] (**5**) [Equation (1)]. Suitable crystals of **5** were obtained from dichloromethane. Complex **5** crystallised as a cross-linked dimer [Zn(bpa^{tBu2,Me2})Cl]$_2$ (Figure 3). Selected bond lengths and bond angles of **5** are summarised in Table 2.



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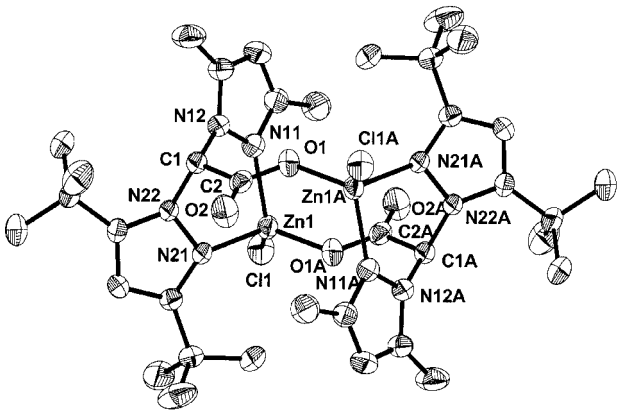


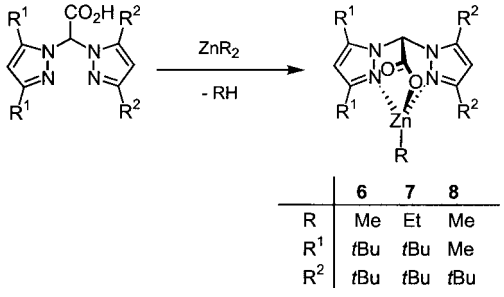
Figure 3. Molecular structure of $[Zn(bpa^{tBu2,Me2})Cl]_2$ (**5**); thermal ellipsoids are drawn at the 50% probability level

Table 2. Selected bond lengths and angles of complex **5**

Distance [Å]	**5**	Angle [°]	**5**
Zn(1)−N(11)	2.031(3)	N(11)−Zn(1)−N(21)	95.17(10)
Zn(1)−N(21)	2.095(2)	O(1A)−Zn(1)−N(11)	112.43(9)
Zn(1)−O(1A)	1.942(2)	O(1A)−Zn(1)−N(21)	103.95(9)
Zn(1)−Cl(1)	2.233(2)	N(11)−Zn(1)−Cl(1)	109.77(8)
		N(21)−Zn(1)−Cl(1)	115.91(6)
		O(1A)−Zn(1)−Cl(1)	117.42(9)

The coordination sphere around the zinc atom is almost tetrahedral, although the angle N(11)−Zn−N(21) [95.17(10)°] is smaller than the ideal tetrahedral one would be. Nevertheless, this tetrahedron is less flattened compared to that previously observed in the structure of the monomer [Zn(bd*t*bpza)Cl].[8] The coordination of the carboxylate group to the zinc atom is less of an *anti*- and more of a *syn*-type compared with the structure of [Zn(bd*t*bpza)Cl].[8] The better donor properties of this *syn*-type coordination may explain the high $\nu_{as}(CO_2^-)$ absorption around 1696 cm^{-1} (KBr pellet). This $\nu_{as}(CO_2^-)$ absorption is rather broad in solution and is found at 1687 cm^{-1}. An IR signal at 1468 cm^{-1} is assigned to $\nu_s(CO_2^-)$. The proposal of a *syn*-type coordination is also supported by a significantly shorter Zn−O(1) distance [1.942(2) Å] and a longer Zn−Cl distance [2.233(2) Å] compared to those in [Zn(bd*t*bpza)Cl] [1.990(2) and 2.170(2) Å].[8] Again, two sets of signals are observed in the NMR spectra due to the two different pyrazolyl groups. Not all of the quaternary signals are detected in the ^{13}C NMR spectrum that might be caused by a monomer/dimer equilibrium.

In the presence of Lewis base type ligands such as pyridine (py) an equimolar amount of acetic acid selectively cleaves one of the Zn−C bonds of dimethylzinc to form methane and the dimer $[Zn(OAc)(CH_3)(py)]_2$.[17] We have observed, that with sterically demanding bis(pyrazol-1-yl)-acetic acids, monomeric four-coordinated alkyl[bis(pyrazol-1-yl)acetato]zinc complexes are obtained in a similar way. Thus, reaction of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (**2**) with dialkylzinc ZnR_2 (R = CH_3, CH_2CH_3) generates alkylzinc complexes [Zn(bd*t*bpza)(CH_3)] (**6**) and [Zn(bd*t*bpza)(CH_2CH_3)] (**7**) [Equation (2)] with the elimination of alkane.



(2)

	6	**7**	**8**
R	Me	Et	Me
R^1	*t*Bu	*t*Bu	Me
R^2	*t*Bu	*t*Bu	*t*Bu

Earlier studies by H. Vahrenkamp et al.[18] and G. Parkin et al.[19] have already shown that four-coordinated alkyl[hydrotris(pyrazol-1-yl)borato]zinc complexes can be obtained by metathesis of ZnR_2 with potassium or thallium salts of sterically demanding hydrotris(pyrazol-1-yl)borate ligands. Since bis(pyrazol-1-yl)acetic acid, and not an alkali carboxylate ligand salt, was used for this synthesis, the workup procedure was simple and **6** and **7** were obtained in high yield and purity; [Zn(bd*t*bpza)(CH_3)] (**6**) is characterised by resonances attributed to the Zn−Me group at δ = −0.35 ppm (^1H NMR) and δ = −10.1 ppm (^{13}C NMR). For the Zn−Et group of [Zn(bd*t*bpza)(CH_2CH_3)] (**7**) signals are found in the ^1H NMR spectrum at δ = 0.52 ppm (q, $^3J_{H,H}$ = 8.0 Hz, CH_2) and δ = 1.29 ppm (t, $^3J_{H,H}$ = 8.0 Hz, CH_3) and in the ^{13}C NMR spectrum at δ = 3.3 ppm (CH_2) and δ = 11.9 ppm (CH_3). The remaining resonances of **6** and **7** can be assigned to the bis(3,5-di-*tert*-butylpyrazol-1-yl)acetato ligand. The analogous reaction of (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid ($bpaH^{tBu2,Me2}$) (**4**) with dimethylzinc gave the chiral methylzinc complex $[Zn(bpa^{tBu2,Me2})(CH_3)]$ (**8**) [Equation (2)]. The resonances attributed to the Zn−Me group are observed at δ = −0.42 ppm (^1H NMR) and δ = −14.1 ppm (^{13}C NMR). In the infrared spectrum the $\nu_{as}(CO_2^-)$ absorption is assigned to a band at 1669 cm^{-1} and $\nu_s(CO_2^-)$ is assigned to a band at 1466 cm^{-1}. Two sets of NMR and IR signals are found for the two different pyrazolyl groups of the (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetato ligand. Complex **8** was obtained as a racemic mixture of a chiral complex. Crystals of **8** suitable for X-ray structure determination were obtained from a racemic solution of **8** in CH_2Cl_2. The structure of complex **8** represents one of the rare examples of monomeric four-coordinated alkylzinc complexes and is the first with a carboxylate *O*-donor ligand. Monomers of both enantiomers crystallised in the cell as a result of the centrosymmetric space group (Figure 4). Selected bond lengths and bond angles of **8** are summarised in Table 3.

The Zn−CH_3 bond length in complex **8** [1.962(8) Å] is similar to that in $[Zn(CH_3)Tp^{Me2}]$ [1.981(8) Å].[19] The most striking features of the molecular structure of **8** are

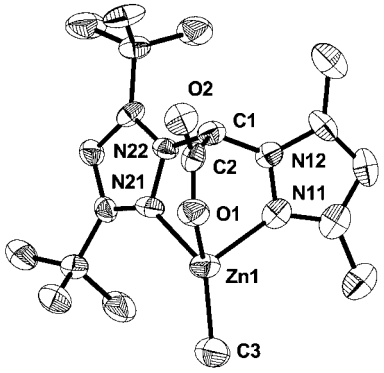


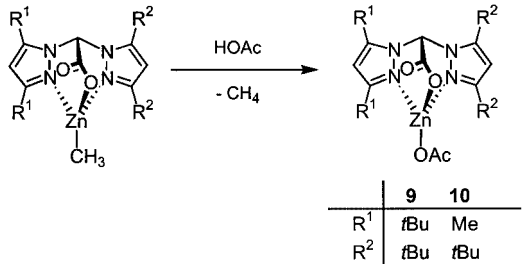
Figure 4. Molecular structure of [Zn(bpa^{tBu2,Me2})(CH$_3$)] (**8**); thermal ellipsoids are drawn at the 50% probability level

Table 3. Selected bond lengths and angles of complex **8**

Distance [Å]	**8**	Angle [°]	**8**
Zn(1)−N(11)	2.085(7)	N(11)−Zn(1)−N(21)	88.3(3)
Zn(1)−N(21)	2.104(6)	O(1)−Zn(1)−N(11)	88.5(2)
Zn(1)−O(1)	2.054(6)	O(1)−Zn(1)−N(21)	87.0(2)
Zn(1)−C(3)	1.962(8)	C(3)−Zn(1)−N(11)	119.8(3)
		C(3)−Zn(1)−N(21)	133.1(3)
		C(3)−Zn(1)−O(1)	126.8(3)

the two different angles C(3)−Zn−N(11) [119.8(3)°] and C(3)−Zn−N(21) [133.1(3)°]. Obviously, the methyl group C(3) is avoiding the bulky *tert*-butyl group. This implies a possible stereoselective induction for future alkyl-transfer reactions.

The reactivity of **6** and **8** towards acetic acid has been examined to provide acetato complexes as useful precursors to enzyme models. A slight excess of acetic acid cleaves the Zn−CH$_3$ bond with the elimination of methane and yields [Zn(OAc)(bd*t*bpza)] (**9**) and [Zn(OAc)(bpa^{tBu2,Me2})] (**10**) [Equation (3)].



(3)

Therefore, **6** and **8** exhibit a reactivity similar to that of [Zn(CH$_3$)(Tp^{Ph})] and [Zn(CH$_3$)(Tp^{tBu})].[18,19] Signals at δ = 2.12 ppm in the ^{1}H NMR and δ = 21.1 ppm in the ^{13}C NMR spectra of **9** are assigned to the methyl group of the acetato ligand. The carboxylate signal of the acetato ligand was found at δ = 178.2 ppm in the ^{13}C NMR spectrum. Most of the NMR signals of **9** are broad compared to those of the recently published [Zn(bd*t*bpza)Cl] complex. These broad resonances may indicate an η^1/η^2 equilibrium of the acetato ligand. Two additional IR signals at 1633 cm^{-1} and 1602 cm^{-1} are therefore assigned to $\nu_{as}(CO_2^-)$ of η^1- and η^2-bound acetato ligands. The IR signals at 1681 cm^{-1} and 1467 cm^{-1} are assigned to $\nu_{as}(CO_2^-)$ and $\nu_s(CO_2^-)$ of the bd*t*bpza ligand. This is proof of the monomeric structure of **9**, since the monomer [Zn(bd*t*bpza)Cl] shows a similar $\nu_{as}(CO_2^-)$ signal at 1681 cm^{-1}.[8] The value of $\Delta\nu_{as\text{-}s}$ indicates the binding mode of the carboxylate ligand. Values of $\Delta\nu_{as\text{-}s} \geq 200$ cm^{-1} are typical for a unidentate binding mode of acetates which is in good agreement with the $\Delta\nu_{as\text{-}s}$ values of the bis(pyrazol-1-yl)acetato ligands in the complexes **5**−**9**.[20]

The NMR spectra of the complex [Zn(OAc)(bpa^{tBu2,Me2})] (**10**) formed in benzene are similar to those of **9** although two sets of signals for the two different pyrazolyl groups are visible. Three ^{1}H NMR signals at δ = 2.10 ppm, δ = 2.36 ppm and δ = 2.49 ppm are ascribed to two methyl groups of the bpa^{tBu2,Me2} ligand and one of the acetato ligand. A resonance at δ = 22.1 ppm in the ^{13}C NMR spectrum is assigned to the methyl group of the acetato ligand. The carboxylate signal of the acetato ligand was found at δ = 181.2 ppm in the ^{13}C NMR spectrum of **10**. Most of the NMR signals of **10** are broader than those of **9**. Quaternary carbon atoms are difficult to detect in the ^{13}C NMR spectrum due to the signals being broad. A ^{1}H NMR spectrum at −70 °C shows two sets of signals, again indicating an η^1/η^2 equilibrium of the acetato ligand. These slight differences compared with **9** might be explained by the fact that complex **10** is sterically less hindered. In addition to two acetato $\nu_{as}(CO_2^-)$ absorptions at 1624 cm^{-1} and 1601 cm^{-1}, weak IR signals are visible at 1442 cm^{-1} and 1427 cm^{-1} which might be assigned to $\nu_s(CO_2^-)$. The resulting $\Delta\nu_{as\text{-}s}$ values of 159 cm^{-1} and 197 cm^{-1} also verify an η^1/η^2 equilibrium.

[Zn(OAc)(bd*t*bpza)] (**9**) and [Zn(OAc)(bpa^{tBu2,Me2})] (**10**) may also be prepared by reaction of bd*t*bpzaH (**2**) or (bpaH^{tBu2,Me2}) (**4**) with Zn(OAc)$_2$ or from the reaction of

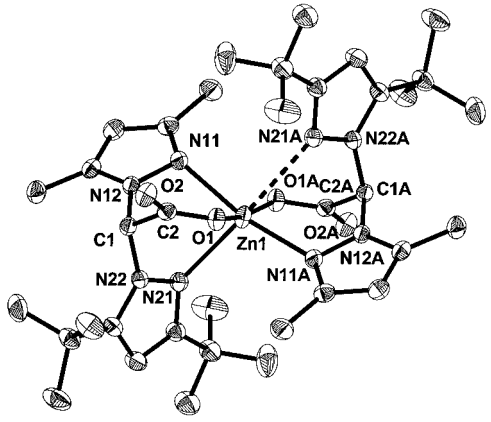


Figure 5. Molecular structure of [Zn(bpa^{tBu2,Me2})$_2$] (**11**); thermal ellipsoids are drawn at the 50% probability level; only one of the zinc positions is shown

the chloro complexes [Zn(bd*t*bpza)Cl] or [Zn(bpa^{tBu2,Me2})Cl] (**5**) with silver acetate. Due to a more complicated workup in these routes along with the formation of by-products we prefer the alkylzinc route.

During the synthesis of **10** in an acetonitrile solution a sandwich complex [Zn(bpa^{tBu2,Me2})$_2$] (**11**) was formed as a by-product. The facile formation of the related six-coordinated complexes [Zn(Tp^R)$_2$] in the reactions of [Zn(Tp^R)X] (X = OH, CH_3, Cl) has already been reported by H. Vahrenkamp et al.,[18] G. Parkin et al.[19] and Kläui et al.[21] with either octahedral[19] or tetrahedral[21] structures of the complexes [Zn(Tp^R)$_2$]. This redistribution seems to be favoured by polar solvents and sterically less demanding ligands, since the synthesis of [Zn(OAc)(bd*t*bpza)] (**9**) is less problematic. Crystals of compound **11** suitable for X-ray analysis were obtained from a solution in $CHCl_3$ (Figure 5). Bond lengths and bond angles of **11** are summarised in Table 4.

Table 4. Selected bond lengths and angles of complex **11**

Distance [Å]	**11**	Angle [°]	**11**
Zn(1)−N(11)	2.156(3)	N(11)−Zn(1)−N(21)	83.99(9)
Zn(1)−N(21)	2.3456(17)	O(1)−Zn(1)−N(11)	86.66(10)
Zn(1)−N(21A)	2.7319(18)	O(1)−Zn(1)−N(21)	89.62(8)
Zn(1)−O(1)	2.006(3)		
Zn(1)−Zn(1A)	0.405(2)		

A structural model with the zinc atom in the centre of the symmetry resembled that of [Zn(bdmpza)$_2$], which we reported recently.[8] The main differences were the extraordinary long bonds of the Zn atom to each of the nitrogen atoms of the two 3,5-di-*tert*-butylpyrazol-1-yl rings. This distance Zn−N(21) [2.5369(14) Å] was in between that of [Zn(bdmpza)$_2$] [2.180(3) Å] and the sum of the van der Waals radii [N 1.55 Å; Zn 1.40 Å]. Until now examples of octahedral zinc complexes with a longer Zn−N distance were rare, and in most cases were caused by a disorder.[22] In addition to the long bond the thermal ellipsoid of the zinc atom is rather elongated towards the two 3,5-di-*tert*-butylpyrazol-1-yl rings. Therefore, the zinc atom in **11** is disordered with two equally occupied positions slightly off the centre of symmetry; **11** exhibits a distorted square-pyramidal coordination with the 3,5-di-*tert*-butylpyrazol-1-yl group slightly bent away from the Zn−N(21) axis and the other 3,5-di-*tert*-butylpyrazol-1-yl group has a weak interaction with the zinc ion from the base direction of the pyramid.

Conclusions

A synthetic route to a racemic mixture of the new chiral scorpionate ligand (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid (**4**) was found via 3,5-di-*tert*-butyl-1-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole (**3**). It is sterically less hindered than the recently published bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (**2**), but its coordination properties are similar to those of **2**. The reaction of **2** or **4** with dialkylzinc yields the new alkylzinc complexes [Zn(bd*t*bpza)(CH_3)] (**6**), [Zn(bd*t*bpza)(CH_2-CH_3)] (**7**) and [Zn(bpa^{tBu2,Me2})(CH_3)] (**8**). Complex **8** is an example of rare monomeric alkylzinc complexes and is the first one with a carboxylate *O*-donor ligand. Acetato complexes [Zn(OAc)(bd*t*bpza)] (**9**) and [Zn(OAc)(bpa^{tBu2,Me2})] (**10**), that serve as models for the active sites of the zinc-containing enzymes carboxypeptidase A or thermolysin, were obtained by reaction of **6** and **8** with acetic acid. Future work has to define a synthetic way to obtain enantiomerically pure bis(pyrazol-1-yl)acetic acids and has to prove whether the configuration of these is stable. This might be useful for structural model complexes of metalloenzymes as well as for organometallic complexes with bis(pyrazol-1-yl)acetate ligands. The first examples of manganese, rhenium and ruthenium complexes with non-chiral bis(pyrazol-1-yl)acetate ligands have already been published.[23]

Experimental Section

General: All experiments were carried out in Schlenk tubes using suitable purified solvents. Microcrystalline precipitates were separated by centrifugation with a Hettich Rotina 46 R Schlenk tube centrifuge. IR: Biorad FTS 60, CaF_2 cuvets (0.5 mm). ^1H and ^{13}C NMR: Bruker WM 250, Bruker AC 250, JEOL GX 400, δ values relative to TMS; in some cases the ^{13}C NMR signals of quaternary carbon atoms were too weak to be detected. EI-MS and FAB MS: modified Finnigan MAT 312. Elemental analyses: Analytical Laboratory of the Fachbereich Chemie, Universität Konstanz. A modified Siemens P4 diffractometer was used for X-ray structure determinations. 3,5-Dimethylpyrazole, 2,2,6,6-tetramethyl-3,5-heptanedione, Zn(CH_3)$_2$ solution, Zn(CH_2CH_3)$_2$ solution and $ZnCl_2$ were used as purchased. 1-Chloromethyl-3,5-dimethylpyrazole hydrochloride was synthesised according to the literature.[24] 3,5-Di-*tert*-butylpyrazole was obtained by a standard literature method from 2,2,6,6-tetramethyl-3,5-heptanedione and hydrazine hydrate.[25] The synthesis of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (bd*t*bpzaH) (**2**) via bis(3,5-di-*tert*-butylpyrazol-1-yl)methane (**1**) was reported recently.[8]

Ligand Syntheses

Synthesis of 3,5-Di-*tert*-butyl-1-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole (bpm^{tBu2,Me2}) (3): 3,5-Dimethylpyrazole (6.93 g, 72.1 mmol), 3,5-di-*tert*-butylpyrazole (13.0 g, 72.1 mmol), KOH (8.42 g, 150 mmol), K_2CO_3 (20.7 g, 150 mmol) and benzyltriethylammonium chloride (2.00 g) were dissolved in dichloromethane (300 mL) and heated under reflux for 12 h. Salts were removed by filtration and the filtrate was concentrated in vacuo to dryness. The white residue was dissolved in water and extracted with pentane (4 × 200 mL). The organic layer was dried (Na_2SO_4) and the solvent removed in vacuo yielding a crude mixture of bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm), bis(3,5-di-*tert*-butylpyrazol-1-yl)methane (bd*t*bpzm) (**1**) and 3,5-di-*tert*-butyl-1-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole (bpm^{tBu2,Me2}) (**3**). Column chromatography with pentane on silica (20 cm) yielded a fraction of bd*t*bpzm (**1**) and with pentane/ethyl acetate (14:1) a pure fraction of bpm^{tBu2,Me2} (**3**). The solutions were dried (Na_2SO_4) and solvents were evaporated; bd*t*bpzm (yield 8.52 g, 63%) was used as described earlier to synthesise bd*t*bpza (**3**).[8] The white residue of

bpm^{tBu2,Me2} (**3**) was recrystallised from acetone to give **3** as colourless crystals, which were dried in vacuo. R_f (pentane/ethyl acetate, 14:1, v/v, silica 60 plate, ammonium vanadate stain) = 0.78 [bd*t*bpzm (**1**)], 0.30 [bpm^{tBu2,Me2} (**3**)]; yield (**3**) 3.52 g (17%); m.p. 75 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.25 (s, 9 H, CH_3), 1.37 (s, 9 H, CH_3), 2.18 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 5.78 (s, 1 H, H_{pz}), 5.86 (s, 1 H, H_{pz}), 6.27 (s, 2 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 11.4 (CH_3), 13.4 (CH_3), 30.3 (CH_3), 30.4 (CH_3), 31.6 (C-*t*Bu), 31.9 (C-*t*Bu), 63.1 (CH_2), 101.0 (C_{pz}), 106.5 (C_{pz}), 141.2 (C_{pz}), 147.6 (C_{pz}), 152.6 (C_{pz}), 160.1 (C_{pz}) ppm. EI MS (70 eV): *m*/*z* (%) = 288 (26) [M^+], 193 (30) [$M^+ - C_5H_7N_2$], 108 (100) [$M^+ - C_{11}H_{19}N_2$]. IR (THF): $\tilde{\nu}$ = 1559 (C=N), 1541 (C=N) cm^{-1}. $C_{17}H_{28}N_4$ (288.44): calcd. C 70.79, H 9.78, N 19.42; found C 70.99, H 9.88, N 19.17. Reaction of 1-chloromethyl-3,5-dimethylpyrazole hydrochloride with 1 equiv. of 3,5-di-*tert*-butylpyrazole, traces of benzyltriethylammonium chloride and excess of KOH and K_2CO_3 in THF yielded an identical sample of **3**.

Synthesis of (3,5-Di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic Acid (bpaH^{rBu2,Me2}) (4): A solution of 3,5-di-*tert*-butyl-1-[(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl]-1*H*-pyrazole (bpm^{tBu2,Me2}) (**3**) (6.50 g, 22.5 mmol) in THF (100 mL) was treated with *n*BuLi (ca. 1.6 M solution in hexane, 15.0 mL, 24.0 mmol) at −70 °C. The solution was heated to −45 °C over a period of 2 h and finally flushed with a flow of carbon dioxide. At ambient temperature, the solvent was removed in vacuo and the white residue dissolved in water (100 mL). The aqueous solution was acidified with concentrated HCl to a pH value of 1 and extracted with diethyl ether (4 × 200 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to give a white residue. The residue was washed with pentane (2 × 200 mL) to remove unchanged bpm^{tBu2,Me2} (**3**) and dried in vacuo to yield (3,5-di-*tert*-butylpyrazol-1-yl)(3′,5′-dimethylpyrazol-1-yl)acetic acid (bpaH^{tBu2,Me2}) (**4**) as a colourless powder. Yield 4.00 g (53%); m.p. 172 °C (dec.). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.25 (s, 9 H, CH_3), 1.28 (s, 9 H, CH_3), 2.11 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 5.82 (s, 1 H, H_{pz}), 5.98 (s, 1 H, H_{pz}), 7.14 (s, 1 H, CH), 11.09 (br. s, 1 H, CO_2H) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 11.5 (CH_3), 13.1 (CH_3), 30.1 (CH_3), 30.3 (CH_3), 31.6 (C-*t*Bu), 32.1 (C-*t*Bu), 72.6 (CH), 102.0 (C_{pz}), 108.1 (C_{pz}), 141.3 (C_{pz}), 148.6 (C_{pz}), 154.7 (C_{pz}), 160.3 (C_{pz}), 166.1 (CO_2H) ppm. EI MS (70 eV, 160 °C): *m*/*z* (%) = 332 (7) [M^+], 288 (20) [$M^+ - CO_2$], 193 (100) [$M^+ - C_5H_7N_2 - CO_2$], 109 (58) [$M^+ - C_{11}H_{19}N_2 - CO_2$], 57 (20) [$C_4H_9$]. IR (THF): $\tilde{\nu}$ = 1758 (CO_2H), 1560 (C=N), 1546 (C=N) cm^{-1}. $C_{18}H_{28}N_4O_2$ (332.45): calcd. C 65.03, H 8.49, N 16.85; found C 64.79, H 8.76, N 16.31.

Synthesis of Model Compounds

Synthesis of [Zn(bpa^{rBu2,Me2})Cl]$_2$ (5): $ZnCl_2$ (200 mg, 1.47 mmol) was added to a solution of (3,5-di-*tert*-butylpyrazol-1-yl)(3,5-dimethylpyrazol-1-yl)acetic acid (bpaH^{tBu2,Me2}) (**4**) (400 mg, 1.20 mmol) in acetonitrile (30 mL), and the solution was stirred vigorously at ambient temperature. After 5 min, potassium *tert*-butoxide (135 mg, 1.20 mmol) was added. Within 1 min, a white precipitate formed. After 2 h, the solvent was removed in vacuo. The residue was dissolved in dichloromethane (15 mL) and salts were separated by centrifugation or filtration through Celite. Dichloromethane was removed in vacuo, the residue washed with diethyl ether (2 × 10 mL) and dried in vacuo to afford [Zn(bpa^{tBu2,Me2})Cl]$_2$ (**5**) as a white crystal powder. An air-exposed solution in dichloromethane at room temperature yielded, within 1 d, prism-like colourless crystals suitable for X-ray structure determination. Yield 390 mg (75%); m.p. 259 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.37 (s, 9 H, CH_3), 1.48 (s, 9 H, CH_3), 2.47 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 6.00 (s, 1 H, H_{pz}), 6.09 (s, 1 H, H_{pz}), 6.82 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 11.5 (CH_3), 13.6 (CH_3), 30.1 (CH_3), 30.4 (CH_3), 31.6 (C-*t*Bu), 32.5 (C-*t*Bu), 70.0 (CH), 103.1 (C_{pz}), 107.8 (C_{pz}), four C_{pz} signals not detected, 164.6 (CO_2^-) ppm. EI MS (70 eV, 270 °C): *m*/*z* (%) = 430 (2) [M^+], 386 (48) [$M^+ - CO_2$], 329 (100) [$M^+ - CO_2 - C_4H_9$], 290 (22) [$M^+ - C_5H_8N_2 - CO_2$], 108 (39) [$C_6H_8N_2$]. IR (CH_2Cl_2): $\tilde{\nu}$ = 1687 br (*as*-CO_2^-), 1561 (C=N), 1548 (C=N), 1468 (*s*-CO_2^-) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 1696 (*as*-CO_2^-), 1558 (C=N), 1547 (C=N), 1467 (*s*-CO_2^-) cm^{-1}. $C_{18}H_{27}ClN_4O_2Zn$ (432.27): calcd. C 50.01, H 6.30, N 12.96; found C 49.86, H 6.51, N 12.68.

Method A. General Procedure for Bis(pyrazol-1-yl)acetato(alkyl)-zinc Complexes: A solution of a sterically demanding bis(pyrazol-1-yl)acetic acid in diethyl ether was added to a slight excess of dialkylzinc in diethyl ether. Gas evolution was observed. The solution was stirred at ambient temperature for 1 h. After this time, gas evolution had ceased and the solvent was evaporated. The white residue was dissolved in CH_2Cl_2 or benzene and filtered through Celite. The solvent was again removed in vacuo to yield the product as a white residue.

Synthesis of [Zn(bd*t*bpza)(CH$_3$)] (6): Reaction of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (bd*t*bpzaH) (**2**) (500 mg, 1.20 mmol) in diethyl ether (10 mL) with $Zn(CH_3)_2$ (0.620 mL of a 2 M solution in toluene, 1.24 mmol) in diethyl ether (10 mL) according to Method A and subsequent workup with CH_2Cl_2 (20 mL) yielded product **6** as a white residue. Yield 550 mg (92%); m.p. 229 °C (dec.). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = −0.35 (s, 3 H, CH_3), 1.36 (s, 18 H, CH_3), 1.53 (s, 18 H, CH_3), 6.08 (s, 2 H, H_{pz}), 7.32 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = −10.1 (CH_3-Zn), 30.2 (CH_3), 31.2 (CH_3), 32.0 (C-*t*Bu), 32.3 (C-*t*Bu), 72.1 (CH), 103.1 (C_{pz}), 155.1 (C_{pz}), 163.1 (C_{pz}), 166.3 (CO_2^-) ppm. EI MS (70 eV, 180 °C): *m*/*z* (%) = 481 (18) [$M^+ - CH_3$], 452 (8) [$M^+ - CO_2$], 435 (100) [$M^+ - C_4H_9$], 393 (83) [$M^+ - CO_2 - C_4H_9$], 371 (71) [$M^+ - Zn - CH_3 - CO_2$], 321 (12) [$M^+ - Zn - CH_3 - CO_2 - 2\ C_4H_9$], 57 (62) [$C_4H_9$]. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1673 (*as*-CO_2^-), 1543 (C=N), 1465 (*s*-CO_2^-) cm^{-1}. $C_{25}H_{42}N_4O_2Zn$ (496.01): calcd. C 60.54, H 8.53, N 11.30; found C 60.50, H 8.72, N 11.30.

Synthesis of [Zn(bd*t*bpza)(CH$_2$CH$_3$)] (7): Reaction of bis(3,5-di-*tert*-butylpyrazol-1-yl)acetic acid (bd*t*bpzaH) (**2**) (500 mg, 1.20 mmol) in diethyl ether (20 mL) with $Zn(CH_2CH_3)_2$ (1.30 mL of a 1 M solution in hexane, 1.30 mmol) in diethyl ether (10 mL) according to Method A and subsequent workup with CH_2Cl_2 (20 mL) yielded product **7** as a white residue. Yield 502 mg (82%); m.p. 168−170 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.52 (q, $^3J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 1.29 (t, $^3J_{H,H}$ = 8.0 Hz, 3 H, CH_3), 1.35 (s, 18 H, CH_3), 1.52 (s, 18 H, CH_3), 6.06 (s, 2 H, H_{pz}), 7.30 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 3.3 (CH_2), 11.9 (CH_3), 30.2 (CH_3), 31.2 (CH_3), 32.0 (C-*t*Bu), 32.3 (C-*t*Bu), 72.1 (CH), 103.1 (C_{pz}), 155.1 (C_{pz}), 163.0 (C_{pz}), 166.6 (CO_2^-) ppm. EI MS (70 eV, 240 °C): *m*/*z* (%) = 479 (40) [$M^+ - CH_2CH_3$], 435 (96) [$M^+ - CH_2CH_3 - CO_2$], 407 (56) [$M^+ - CO_2 - C_4H_9$], 371 (100) [$M^+ - CH_2CH_3 - CO_2 - Zn$], 321 (14) [$M^+ - CH_2CH_3 - CO_2 - Zn - 2\ C_4H_9$], 193 (53) [$C_{12}H_{21}N_2$], 57 (43) [$C_4H_9$]. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1671 (*as*-CO_2^-), 1544 (C=N), 1465 (*s*-CO_2^-) cm^{-1}. $C_{26}H_{44}N_4O_2Zn$ (510.04): calcd. C 61.23, H 8.70, N 10.98; found C 60.75, H 8.82, N 10.43.

Synthesis of [Zn(bpa^{rBu2,Me2})(CH$_3$)] (8): Reaction of (3,5-di-*tert*-butylpyrazol-1-yl)(3,5-dimethylpyrazol-1-yl)acetic acid (bpaH^{tBu2,Me2}) (**4**) (0.970 g, 2.92 mmol) in diethyl ether (20 mL) with $Zn(CH_3)_2$ (1.65 mL of a 2 M solution in toluene, 3.30 mmol) in diethyl ether (20 mL) according to Method A and subsequent workup with

CH_2Cl_2 (20 mL) yielded product **8** as a white residue. Yield 1.12 g (93%); m.p. 187 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = −0.42 (s, 3 H, CH_3), 1.38 (s, 9 H, CH_3), 1.52 (s, 9 H, CH_3), 2.30 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 5.99 (s, 1 H, H_{pz}), 6.01 (s, 1 H, H_{pz}), 6.89 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = −14.1 (CH_3-Zn), 11.5 (CH_3), 12.9 (CH_3), 30.3 (CH_3), 30.5 (CH_3), 31.5 (C-*t*Bu), 32.1 (C-*t*Bu), 70.2 (CH), 102.1 (C_{pz}), 107.3 (C_{pz}), 141.6 (C_{pz}), 150.7 (C_{pz}), 154.1 (C_{pz}), 162.7 (C_{pz}), 165.4 (CO_2^-) ppm. FAB MS (NBOH matrix): *m*/*z* (%) = 809 (21) [$M_2H^+ - CH_3$], 763 (10) [$M_2H^+ - CH_3 - CO_2$], 411 (100) [MH^+], 395 (9) [$M^+ - CH_3$], 365 (31) [$M^+ - CO_2H$], 351 (78) [$M^+ - CH_3 - CO_2$], 287 (86) [$M^+ - CH_3 - CO_2 - Zn$]. IR (CH_2Cl_2): $\tilde{\nu}$ = 1669 (*as*-CO_2^-), 1559 (C=N), 1539 (C=N), 1466 (*s*-CO_2^-) cm^{-1}. $C_{19}H_{30}N_4O_2Zn$ (411.85): calcd. C 55.41, H 7.34, N 13.60; found C 55.02, H 7.21, N 13.62.

Method B. General Procedure for Acetato[bis(pyrazol-1-yl)acetato]-zinc Complexes: An excess of acetic acid was added to a solution of a methyl[bis(pyrazol-1-yl)acetato]zinc complex in benzene. Gas evolution was observed. The solution was stirred at ambient temperature for 30 min. After this time, gas evolution had ceased, the solution was filtered through Celite and the volume of the solution was reduced in vacuo to 1 mL. The product was precipitated with hexane and dried in vacuo to yield the product as a white solid.

Synthesis of [Zn(OAc)(bd*t*bpza)] (9): Reaction of [Zn(bd*t*bpza)-(CH_3)] (**6**) (480 mg, 0.968 mmol) in benzene (10 mL) with acetic acid (100%, 70.0 μL, 1.22 mmol) according to Method B afforded [ZnOAc(bd*t*bpza)] (**9**) as a white crystalline powder. A similar result in yield and purity was obtained from an acetonitrile solution. Yield 400 mg (77%); m.p. 109−111 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.37 (s, 18 H, CH_3), 1.53 (s, 18 H, CH_3), 2.12 (s, 3 H, CH_3−Ac), 6.12 (s, 2 H, H_{pz}), 7.36 (s, 1 H, CH) ppm. ^{1}H NMR (C_6D_6, 250 MHz): δ = 1.21 (s, 18 H, CH_3), 1.43 (s, 18 H, CH_3), 1.93 (s, 3 H, CH_3−Ac), 6.01 (s, 2 H, H_{pz}), 7.55 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 21.1 (CH_3-Ac), 29.9 (CH_3), 31.0 (CH_3), 32.0 (C-*t*Bu), 32.3 (C-*t*Bu), 72.6 (CH), 103.4 (C_{pz}), 155.7 (C_{pz}), 163.2 (C_{pz}), 166.0 (CO_2^-), 178.2 (CO_2^-) ppm. ^{13}C NMR (C_6D_6, 62.5 MHz): δ = 21.9 (CH_3-Ac), 30.5 (CH_3), 30.8 (CH_3), 32.2 (C-*t*Bu), 32.4 (C-*t*Bu), 75.0 (CH), 103.0 (C_{pz}), 154.7 (C_{pz}), 161.8 (C_{pz}), 168.5 (CO_2^-), 179.8 (CO_2^-) ppm. EI MS (70 eV, 200 °C): *m*/*z* (%) = 494 (55) [$M^+ - CO_2$], 479 (43) [$M^+ - CO_2CH_3$], 437 (85) [$M^+ - CO_2 - C_4H_9$], 371 (61) [$M^+ - CO_2CH_3 - CO_2 - Zn$], 193 (100) [$C_{12}H_{21}N_2$], 179 (66) [$C_{11}H_{19}N_2$]. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1681 (*as*-CO_2^-), 1633 (*as*-CO_2^-), 1602 (*as*-CO_2^-), 1546 (C=N), 1467 (*s*-CO_2^-) cm^{-1}. $C_{26}H_{42}N_4O_4Zn$ (540.02): calcd. C 57.83, H 7.84, N 10.37; found C 58.00, H 8.20, N 10.98.

Synthesis of [Zn(OAc)(bpa^{rBu2,Me2})] (10): Reaction of [Zn-(bpa^{tBu2,Me2})(CH_3)] (**8**) (400 mg, 0.971 mmol) in benzene (5 mL) with acetic acid (100%, 57.0 μL, 1.00 mmol) according to Method B but without filtration through Celite afforded [Zn(OAc)(bpa^{tBu2,Me2})] (**10**) as a white crystalline powder. Yield 401 mg (91%); m.p.

Table 5. Structure determination details of compounds **4**, **5**, **8** and **11**

	4	**5**	**8**	**11**
Empirical formula	$C_{18}H_{28}N_4O_2$ × 1/3 C_3H_6O	$C_{18}H_{27}ClN_4O_2Zn$ × 1.5 CH_2Cl_2	$C_{19}H_{30}N_4O_2Zn$ × CH_2Cl_2	$C_{18}H_{27}N_4O_2Zn_{0.5}$ × $CHCl_3$
Formula mass	351.80	559.65	496.77	483.49
Crystal colour/habit	colourless plate	colourless column	colourless plate	colourless block
Crystal system	rhombohedral	monoclinic C	monoclinic P	monoclinic P
Space group	*R*-3	*C*2/*c*	$P2_1/c$	$P2_1/n$
a [Å]	17.691(3)	14.008(14)	11.599(14)	9.8566(4)
b [Å]	17.691(3)	20.489(15)	21.658(17)	22.2125(9)
c [Å]	17.691(3)	19.101(19)	11.130(8)	11.3820(5)
α [°]	115.061(12)	90.00	90.00	90.000(1)
β [°]	115.061(12)	104.15(4)	116.35(8)	112.300(1)
γ [°]	115.061(12)	90.00	90.00	90.000(1)
V [Å^3]	3081.4(22)	5316(8)	2505(4)	2305.60(17)
θ [°]	2.32−27.00	2.20−27.01	2.17−24.01	1.83−28.20
h	−19 to 22	−17 to 17	−13 to 12	−12 to 12
k	−22 to 22	−26 to 26	−1 to 24	−29 to 28
l	−22 to 22	−24 to 24	−1 to 12	−15 to 15
F(000)	1144	2312	1040	1008
Z	6	8	4	4
μ(Mo-K_α) [mm^{-1}]	0.076	1.348	1.215	0.927
Crystal size [mm]	0.5 × 0.3 × 0.15	0.5 × 0.3 × 0.3	0.2 × 0.15 × 0.1	0.3 × 0.2 × 0.2
$D_{calcd.}$ [gcm^{-1}]	1.138	1.399	1.317	1.393
T [K]	188(2)	231(2)	258(2)	143(2)
Reflections collected	9037	11494	4869	36682
Independent reflections	4371	5797	3926	5423
Obsd. refl. ($> 2\sigma I$)	3396	4321	1787	4866
Parameter	242	307	262	262
Weight parameter *a*	0.1050	0.0465	0.0411	0.0527
Weight parameter *b*	2.1776	3.8902	0.2667	1.1558
R_1 (obsd.)	0.0700	0.0412	0.0748	0.0377
R_1 (overall)	0.0868	0.0635	0.1887	0.0421
wR_2 (obsd.)	0.1875	0.0954	0.1155	0.1011
wR_2 (overall)	0.2035	0.1055	0.1512	0.1035
Diff. peak/hole [e/Å^3]	0.812/−0.617	0.497/−0.609	0.316/−0.387	0.681/−0.631

196 °C (dec.). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.33 (s, 9 H, CH_3), 1.51 (s, 9 H, CH_3), 2.10 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3−OAc), 6.00 (s, 1 H, H_{pz}), 6.07 (s, 1 H, H_{pz}), 6.88 (s, 1 H, CH) ppm. ^{1}H NMR (C_6D_6, 250 MHz): δ = 1.24 (s, 9 H, CH_3), 1.36 (s, 9 H, CH_3), 1.92 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3-OAc), 5.39 (s, 1 H, H_{pz}), 5.96 (s, 1 H, H_{pz}), 6.97 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 11.8 (CH_3), 13.1 (CH_3), 22.1 (CH_3-OAc), 30.1 (CH_3), 30.7 (CH_3), 31.8 (C-*t*Bu), 32.3 (C-*t*Bu), 70.5 (CH), 102.9 (C_{pz}), 108.0 (C_{pz}), 142.6 (C_{pz}), 152.3 (C_{pz}), 156.0 (C_{pz}), 164.3 (C_{pz}), 165.1 (CO_2^-), 181.2 (CO_2^-) ppm. EI MS (70 eV, 230 °C): *m*/*z* (%) = 410 (18) [$M^+ - CO_2$], 353 (58) [$M^+ - CO_2 - C_4H_9$], 288 (100) [$M^+ - CO_2 - O_2CCH_3 - Zn$], 193 (30) [$C_{12}H_{21}N_2$], 109 (44) [$C_6H_9N_2$]. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 1677 (*as*-CO_2^-), 1624 (*as*-CO_2^-), 1601 (*as*-CO_2^-), 1562 (C=N), 1544 (C=N), 1467 (*s*-CO_2^-), 1442 (*s*-CO_2^-), 1427 (*s*-CO_2^-) cm^{-1}. $C_{20}H_{30}N_4O_4Zn$ (455.86): calcd. C 52.70, H 6.63, N 12.29; found C 52.55, H 6.51, N 11.74.

Synthesis of [Zn(OAc)(bpa^{rBu2,Me2})] (10) in Acetonitrile: Reaction of [Zn(bpa^{tBu2,Me2})(CH_3)] (**8**) (310 mg, 0.753 mmol) in acetonitrile (5 mL) with acetic acid (100%, 80.0 μL, 1.40 mmol) according to Method B afforded [Zn(OAc)(bpa^{tBu2,Me2})] (**10**) as a white crystalline powder. The spectroscopic data are identical to those of **10** that was obtained in benzene solution. Yield (**10**) 162 mg (47%).

[Zn(bpa^{rBu2,Me2})$_2$] (11): During the synthesis of **10** in acetonitrile a white precipitate formed in the solution that was filtered off. This white residue was dissolved in CH_2Cl_2, filtered through Celite and dried in vacuo to yield [Zn(bpa^{tBu2,Me2})$_2$] (**11**) as a white crystalline powder. Additional purification can be achieved by extraction with CH_2Cl_2 from a water suspension. Crystals suitable for X-ray structure determination were obtained from a solution in $CHCl_3$. Yield 80.0 mg (29%); m.p. 207 °C (dec.). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.08 (s, 9 H, CH_3), 1.53 (s, 9 H, CH_3), 1.92 (s, 3 H, CH_3) 2.42 (s, 3 H, CH_3), 5.86 (s, 1 H, H_{pz}), 5.96 (s, 1 H, H_{pz}), 6.90 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 62.5 MHz): δ = 11.8 (CH_3), 13.1 (CH_3), 30.1 (CH_3), 30.8 (CH_3), 31.6 (C-*t*Bu), 32.3 (C-*t*Bu), 70.5 (CH), 102.6 (C_{pz}), 107.6 (C_{pz}), 140.8 (C_{pz}), 150.8 (C_{pz}), 153.0 (C_{pz}), 163.0 (C_{pz}), 166.4 (CO_2^-) ppm. EI MS (70 eV, 250 °C): *m*/*z* (%) = 684 (0.5) [$M^+ - CO_2$], 353 (2) [$C_{17}H_{28}N_4$ + Zn], 288 (5.5) [$C_{17}H_{28}N_4$], 192 (26) [$C_{12}H_{20}N_2$], 177 (100) [$C_{11}H_{17}N_2$]. IR (CH_2Cl_2): $\tilde{\nu}$ = 1664 (*as*-CO_2^-), 1562 (C=N), 1540 (C=N), 1466 (*s*-CO_2^-) cm^{-1}. $C_{36}H_{54}N_8O_4Zn \cdot 2\,CHCl_3$ (967.01): calcd. C 47.39, H 5.87, N 11.64; found C 47.08, H 6.02, N 11.41.

X-ray Structure Determinations: Single crystals of **4**, **5** and **8** were sealed in glass capillaries at room temperature. A modified Siemens P4 diffractometer was used for data collection (Wyckhoff technique, graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å, scan rate 4−30°min^{-1} in ω). The data set of **11** was collected with a Bruker Smart Apex. The structures were solved using direct methods {Siemens SHELXS-93[26]} and refined with full-matrix least squares against F^2 {Siemens SHELXL-97[26]}. A weighting scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2,0)]/3$. Hydrogen atoms were included in their calculated positions and refined in a riding model. Compound **4** crystallised with one third of an acetone molecule in a special position. The carboxylic proton of **4** was found. In the case of **5** the asymmetric unit is filled by half of a dimer of the molecule. In the asymmetric unit of structure **5** one and a half molecules of dichloromethane were found and refined. The half molecule was found in a special position. One molecule of dichloromethane co-crystallised with **8**. In the case of complex **11** one molecule of $CHCl_3$ crystallised with half of the molecule. All details and parameters of the measurements are summarised in Table 5. The structure pictures were prepared with the program Diamond 2.1c.[27] CCDC-184127 [Zn(bpa^{tBu2,Me2})Cl]$_2$ (**5**), -184128 [Zn(bpa^{tBu2,Me2})(CH_3)] (**8**) and -184129 [Zn(bpa^{tBu2,Me2})$_2$] (**11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Generous financial support by the Fonds der Chemischen Industrie (Liebig-Stipendium to N. B.) and the European Commission (Copernicus 2 Program, Contract no. ICA2-CT-2000−10002) is gratefully acknowledged. Special thanks to Prof. Dr. H. Fischer for support and discussion and also to Prof. Dr. W. A. Schenk for giving us access to a Bruker Smart Apex in Würzburg. We are indebted to Mr. Hägele and Mr. Galetskiy for recording mass spectra.

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[16] Due to otherwise extraordinary long abbreviations for compound **4** and its precursor **3**, the abbreviation system for Tp ligands introduced by S. Trofimenko was transferred to this

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Received May 24, 2002
[I02399]