Biomimetic Zinc Complexes With A New Tripodal Nitrogen-Donor Ligand: Tris[2-(1-methyl-4-tolylimidazolyl)phosphane] ($Pim^{Me,pTol}$)

Wolfgang Kläui,*[a] Claudia Piefer,[a] Gerd Rheinwald,[b] and Heinrich Lang[b]

Dedicated to Prof. Dr. H. Vahrenkamp on the occasion of his 60th birthday

Keywords: Bioinorganic chemistry / Carbonic anhydrase / Zinc / N ligands / Tripodal ligands

The new potentially threefold-chelating ligand tris[2-(1-methyl-4-tolylimidazolyl)]phosphane ($Pim^{Me,pTol}$) has been prepared. The *p*-tolyl substituents on the imidazole rings form a shielded hydrophobic cavity. The first X-ray-structure analysis of this ligand system confirms the proposed structure. The reaction of $Pim^{Me,pTol}$ with ZnX_2 salts (X = Cl, Br, I, NO_3) yields monomeric Zn^{II} complexes. The X-ray crystal structures of $[Pim^{Me,pTol}ZnCl]_2(ZnCl_4)$ and $[Pim^{Me,pTol}ZnNO_3]NO_3$ prove that the Zn^{2+} centres are in a tetrahedral environment with threefold *N*-imidazole coordination. This arrangement mimics the active centre of carbonic anhydrase (CA).

Introduction

Zinc is an essential element in biological systems.[1] Its first biological function was found in the enzyme carbonic anhydrase (CA), a hydrolase which catalyses the hydration of carbon dioxide at physiological pH, according to (Equation 1).

$$CO_2 + 2\,H_2O \overset{CA}{\rightleftharpoons} HCO_3^- + H_3O^+ \quad (1)$$

In the absence of a catalyst, this apparently simple reaction is extremely slow. However, it is imperative to nearly all living organisms that this reaction is fast. CA accelerates the rate of hydration of CO_2 10^7-fold.[2] In order to understand the essential structure and reaction characteristics of bioinorganic systems, small molecular model complexes are a convenient approximation. One model system for CA is based on sterically demanding tris(pyrazolyl)hydroborate (Tp) ligands **A**. This type of ligand forms zinc(II) complexes with structural and functional properties similar to those of the active site of CA. An essential prerequisite for the successful application of such systems is the introduction of bulky groups R, such as *tert*-butyl[3], phenyl[4], *p*-cumyl[5] or *p*-tolyl,[6] in the 3-position of the pyrazolyl rings. The presence of these sterically demanding substituents inhibits the formation of bis-ligand complexes $[Zn(Tp)_2]$ and it forces coordination numbers smaller than six. Whereas *tert*-butyl substituents reduce the coordination number exclusively to four, aryl substituents enable Zn^{II} to extend its coordination sphere to five.[7] In addition, the aryl groups form a hydrophobic pocket around the zinc ion. The hydrophobic surrounding should help the coordinated water in complexes $[TpZnOH_2]$ to become acidic at physiological pH. While with this, the importance of steric factors in CA model systems has been established, it remains unclear whether the negative charge of the Tp ligands is required to stabilise biomimetic zinc complexes. One of the main problems in this context is the sensitivity of Tp ligands toward hydrolysis.

Tris(imidazolyl)phosphane ligands are neutral and hydrolytically stable analogues of the Tp ligands to which they are sterically and electronically very similar. Zinc complexes of tris[2-(4,5-diisopropyl)imidazolyl]phosphane[8] and tris[2-(4,5-di-*n*-propyl)imidazolyl]phosphane[9] have been synthesised. It turned out that these complexes are remarkably different in their efficiency in catalysing the CO_2/HCO_3^- equilibrium. Unfortunately the 1,3-tautomerism in the imidazole rings makes it difficult to assess the geometry of the catalytically active zinc complexes. Knowing that the histidyl-imidazol *N*-ligation to metal ions is ubiquitous in nature, further development of zinc coordination chemistry with other imidazole-derived ligands is obviously desirable.

Until now two tris(imidazolyl)phosphane ligands of type **B** have been prepared (Scheme 1).[10] They have 1,4- rather than 4,5-substituted imidazole rings. While in Tp ligands **A** the 5-methyl groups serve as a protecting unit for the hydrolytically sensitive B−N bonds, the 1-alkyl substituent in **B** is only necessary to suppress the 1,3-tautomerism in the imidazole. These tripodal ligands of type **B** have been described only with bulky alkyl substituents in the 1-position as well as in the 4-position. This can be attributed to the fact that the synthesis of substituted imidazole rings is relatively difficult. Thus, only very few zinc-containing enzyme model complexes incorporating substituted imidazole *N*-donor groups have been reported.

[a] Institut für Anorganische und Strukturchemie I, Heinrich-Heine-Universität Düsseldorf,
Universitätsstraße 1, 40225 Düsseldorf, Germany
Fax: (internat.) + 49-(0)2/111-2287
E-mail: klaeui@uni-duesseldorf.de
[b] Lehrstuhl für Anorganische Chemie, Technische Universität Chemnitz,
Straße der Nationen 62, D-09107 Chemnitz, Germany

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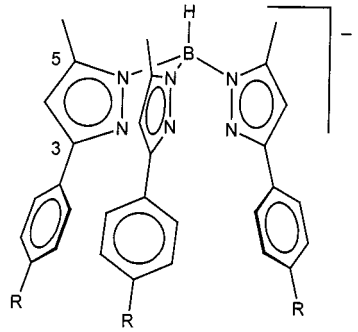
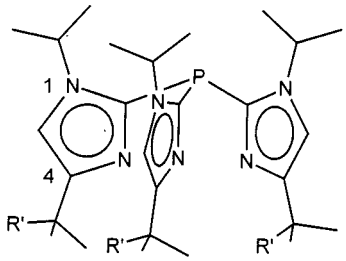


A

R = H, CH_3, $CH(CH_3)_2$



B

R' = H, CH_3

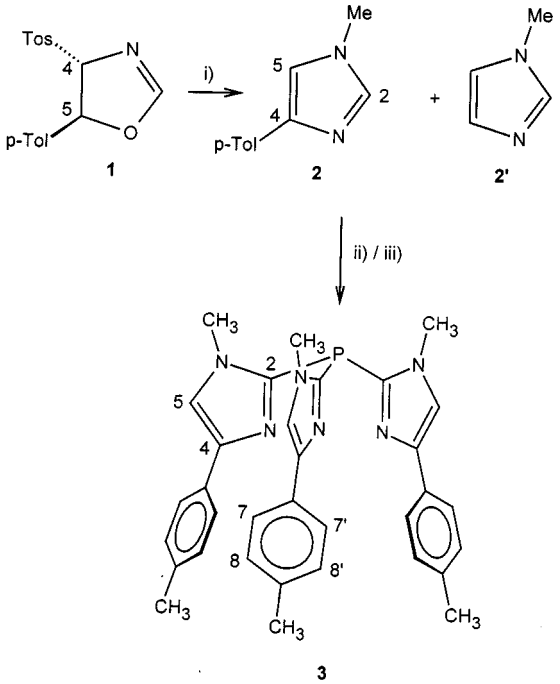
Scheme 1. Schematic structures of aryl-substituted tris(pyrazolyl)-borate ligands and of bulky 1,4-dialkyl-substituted tris(imidazolyl)-phosphane ligands

We describe here the synthesis of the new tripodal *p*-tolyl-substituted tris(imidazolyl)phosphane ligand $Pim^{Me,pTol}$ (**3**) and its reaction behaviour towards Zn^{II} salts in order to develop model systems which can mimic CA enzyme characteristics. This ligand is the first ligand of its type with aryl substituents in the 4-position of the imidazole rings. The aryl substituents were expected to play the same role as in the analogous Tp ligands, i.e. they should form a sterically demanding and hydrophobic cavity around the zinc ion. A bulky isopropyl substituent in the 1-position as in the known ligands $Pim^{iPr,iPr}$ and $Pim^{iPr,tBu}$ [10] seems unnecessary. We have chosen the small methyl group to keep the solubility in protic solvents as high as possible.

Results and Discussion

Synthesis and Spectroscopic Characterisation

The well-established way of preparing tris(imidazolyl)-phosphanes of type **B**[11] was not suitable for synthesising the desired ligand $Pim^{Me,pTol}$ (**3**). Because of the difficulty of introducing an aryl substituent into the imidazole ring regiospecifically, we applied an alternative route, via oxazolines **1**, to prepare the 1,4-disubstituted imidazoles **2**.[12] The mechanism of this reaction did not exclude, a priori, the formation of the second regioisomer **2′**. The isomer **2** as the only product could be confirmed by 2D NMR experiments.[13] Flash chromatography of the reaction mixture afforded crude 1-methyl-4-tolylimidazole in an acceptable yield. In the following step, the imidazole was lithiated in the 2-position and then treated with PCl_3 in THF at −78 °C (Scheme 2) yielding **3** as a colourless solid after crystallisation from dichloromethane/hexane.

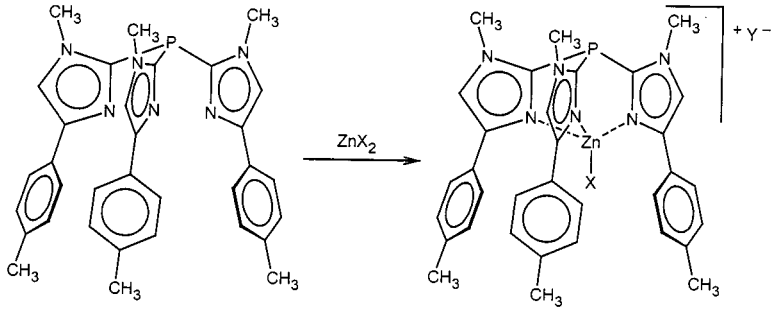


Scheme 2. Synthesis and schematic structure of the aryl-substituted tris(imidazolyl)phosphane ligand $Pim^{Me,pTol}$ (**3**); i) $MeNH_2$ in benzene, autoclave, T = 120 °C, ii) *n*BuLi, THF, −78 °C; iii) PCl_3, THF

The ^1H NMR spectrum of **3** shows C_{3v} symmetry with an $[AB]_2$-system at δ = 7.43 for the *p*-tolyl protons. The doublet at δ = 7.18 ($^3J_{HH}$ = 8 Hz) of the $[AB]_2$-system is assigned to the *m*-protons of the *p*-tolyl group and the doublet at δ = 7.68 ($^3J_{HH}$ = 8 Hz) is assigned to the protons in the *o*-position on the basis of correlated $^1H,^{13}C$ HMBC NMR spectra. The singlet at δ = 7.38 can be assigned to the proton in the 5-position of the substituted imidazole ring and the singlet at δ = 3.76 can be assigned to the protons of the $N-CH_3$ group. In the $^{31}P\{^1H\}$ NMR spectrum of **3** the ^{31}P signal appears at δ = −57.9 as a singlet. The EI mass spectrum of **3** exhibits the peak for the molecular ion at the expected *m/z* value together with a characteristic fragmentation pattern.

The zinc(II) complexes $[Pim^{Me,pTol}ZnX]Y$ were prepared in high yield by stirring the tris(imidazolyl)phosphane **3** with ZnX_2 salts in THF (X = NO_3, Cl, Br) or in ethanol (X = I), under reflux (Scheme 3). The complexes **4a**−**4d** form colourless solids and can be crystallised from acetonitrile or nitromethane to yield analytically pure colourless crystals.

The ^1H NMR spectra of the zinc complexes **4a**−**4d** also show a signal pattern corresponding to C_{3v} symmetry. The signal of the proton in the 5-position of the imidazole ring



4	X	Y
a	Cl	½ $ZnCl_4$
b	Br	Br
c	I	I
d	NO_3	NO_3

Scheme 3. Synthesis and schematic structures of the zinc complexes [$Pim^{Me,pTol}ZnX$]Y (**4a−d)**

is shifted to lower field and split into a doublet (**4a:** δ = 7.53, $^4J_{PH}$ = 4 Hz; **4b:** δ = 7.49, $^4J_{PH}$ = 4 Hz; **4c:** δ = 7.46, $^4J_{PH}$ = 5 Hz; **4d:** δ = 7.56, $^4J_{PH}$ = 4 Hz) when compared to the signal in the free ligand **3**. Upon coordination to Zn^{II}, the ^{31}P signal for complexes **4a−4d** is shifted to higher field (**4a:** δ = −113.7; **4b:** δ = δ = −118.2; **4c:** δ = −119.4; **4d:** δ = −117.8). A similar shift has also been reported for the ^{31}P signal of ligands of type **B** in Cu^I complexes, e.g. [$Pim^{iPr,iPr}CuCH_3CN$][BF_4].[10b] The FAB mass spectra of the Zn^{II} complexes **4a−4d** exhibit the peak for the molecular ion at the expected *m/z* value together with a characteristic fragmentation pattern.

Solid State Structure of 3, 4a and 4d

Crystals of **3** suitable for an X-ray crystal structure determination were obtained by slow evaporation of an acetone solution. It crystallises in the monoclinic space group *Cc* with four independent molecules per unit cell. Crystals of the complexes **4a** and **4d** were grown by diffusion of hexane into a nitromethane solution. Both complexes crystallise in the triclinic space group $P\bar{1}$. The structure of **4a** contains two independent cationic molecules and three solvent molecules of nitromethane per unit cell. The two independent cationic molecules differ only within the ranges of standard deviations, except for one Zn−N distance and some torsion angles.[14] Crystals of **4d** contain one strongly disordered

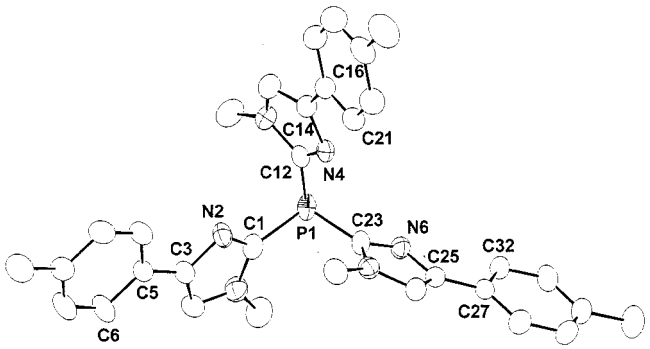


Figure 1. ZORTEP plot[25] (50% probability) of $Pim^{Me,pTol}$ (**3**)

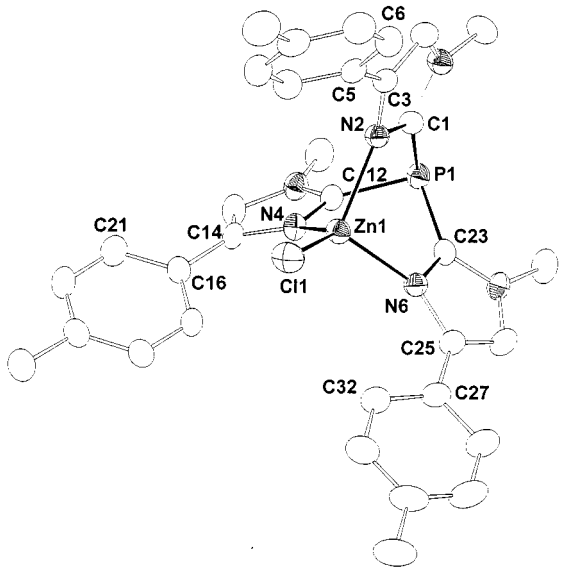


Figure 2. ZORTEP plot[25] (50% probability) of $[Pim^{Me,pTol}ZnCl]^+$ in **4a**

nitromethane molecule. The solid-state structure of the ligand **3** is shown in Figure 1, the structure of the cation $[Pim^{Me,pTol}ZnCl]^+$ of **4a** in Figure 2 and the structure of $[Pim^{Me,pTol}ZnNO_3]^+$ of **4d** is presented in Figure 3. Selected bond length, angles and torsion angles are given in Table 1. The structure of the free ligand **3** is the first solid-state structure reported for a tris(imidazolyl)phosphane ligand.

Figure 1 shows a trigonal pyramidal environment of P(1) with P−C σ-bond lengths and C−P−C bond angles comparable to those of aromatic phosphanes such as tri-*o*-tolylphosphane[15] or tri-*m*-tolylphosphane.[16] The P−C σ-bond lengths of **3** (1.813−1.841 Å) are similar to those found for tri-*o*-tolylphosphane[15] (1.830−1.837 Å) or tri-*m*-tolylphosphane[16] (1.829−1.838 Å). Only one C−P−C bond angle [96.8(2)°] is smaller than those found for tri-*o*-tolylphosphane[15] (101.6−103.4°) or tri-*m*-tolylphosphane[16] (100.6−102.2°). The small deviation of the N−C−C−C bond torsion angles of **3** (Table 1) from 0° or 180°, respectively, indicates that the *p*-tolyl rings are nearly coplanar with the imidazolyl-system in the free ligand.

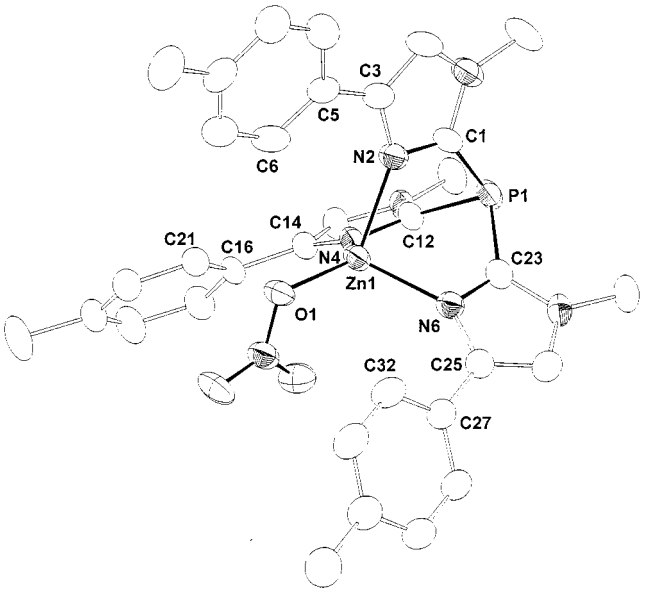


Figure 3. ZORTEP plot[25] (50% probability) of $[Pim^{Me,pTol}ZnNO_3]^+$ in **4d**

Table 1. Selected bond distances (Å), angles (°) and torsion angles (°) for $Pim^{Me,pTol}$ (**3**), $[Pim^{Me,pTol}ZnCl]^+$ in **4a**, and $[Pim^{Me,pTol}ZnNO_3]^+$ in **4d**

	3	**4a**	**4d**
Zn(1)−N(6)		2.074(3)	2.025(2)
Zn(1)−N(4)		2.057(3)	2.026(2)
Zn(1)−N(2)		2.062(3)	2.092(2)
P(1)−C(1)	1.841(5)	1.818(4)	1.817(3)
P(1)−C(12)	1.824(5)	1.824(4)	1.825(3)
P(1)−C(23)	1.813(5)	1.812(4)	1.828(3)
N(4)−Zn(1)−N(2)		95.75(12)	93.97(9)
N(6)−Zn(1)−N(2)		99.89(11)	95.44(9)
N(6)−Zn(1)−N(4)		90.29(12)	100.23(9)
C(1)−P(1)−C(12)	96.8(2)	97.36(16)	95.61(13)
C(1)−P(1)−C(23)	103.5(2)	98.71(17)	97.29(14)
C(12)−P(1)−C(23)	102.2(2)	97.57(16)	100.42(13)
N(2)−C(3)−C(5)−C(6)	179.5(5)	141.5(4)	−15.0(5)
N(4)−C(14)−C(16)−C(21)	−15.1(7)	146.5(5)	29.4(4)
N(6)−C(25)−C(27)−C(32)	5.9(6)	14.0(6)	−35.6(5)
Zn(1)−Cl(1)/−O(1)		2.1725(10)	1.9592(19)

The structures of the two cationic Zn^{II} complexes **4a** and **4d** reveal a slightly distorted tetrahedral coordination environment of Zn^{II} with threefold *N*-imidazolyl coordination. The Zn(1)−Cl(1) bond length in **4a** [2.1725(10)Å] does not differ significantly from that of the other known tris(imidazolyl)phosphanezinc chloride complex chloro{tris[2-(4,5-diisopropylimidazolyl)phosphane]}zinc chloride [2.170(2)-Å].[17] The Zn(1)−O(1) bond length [1.9592(19)Å] pertaining to the coordinating NO_3 in **4d** is similar to the Zn−O distances in the nitrato complex tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)phosphane]zinc nitrate [1.986(4)-Å].[10a] The nitrate ligand in complex **4d** acts as a monodentate ligand[18] unlike the coordinating nitrate in tris[2-(1-isopropyl-4-*tert*-butylimidazolyl)phosphane]zinc nitrate which shows an anisobidentate coordination mode. This is surprising in view of the different steric bulk of the *p*-tolyl and *tert*-butyl groups. We expected that the less bulky *p*-tolyl groups would allow for bidentate coordination of the nitrate ligand. The N−Zn−N bond angles in both **4a** (90.3−99.9°) and **4d** (94.0−100.2°) are smaller than the tetrahedral angle. These angles do not differ significantly from previously reported values for tris(imidazolyl)phosphanes, e.g. chloro{tris[2-(4,5-diisopropylimidazolyl)phosphane]}-zinc chloride[17] or $[Pim^{iPr,tBu}ZnX]^+$ (X = OH, I, NO_3).[10a] The three Zn−N bond lengths in the structure **4a** are equal (mean: 2.064 Å) and are very similar to the Zn−N bond lengths in **4d** (2.025−2.092 Å) and $[Pim^{iPr,tBu}ZnX]^+$ (X = OH, I, NO_3).[10a] It is worth mentioning that the Zn−N bond lengths and N−Zn−N bond angles in the analogous hydrotris(pyrazolyl)borate complexes $[Tp^{Me,Ph}ZnNO_3]$[4a] and $[Tp^{Me,Ph}ZnCl]$,[19] do not differ significantly from those found for tris(imidazolyl)phosphanes. The P−C bond lengths of **4a** (mean: 1.818 Å) and **4d** (mean: 1.823 Å) are equivalent within the standard deviation and show no significant differences to those found for the free ligand **3**. The C−P−C bond angles of **4a** (97.4−98.7°) and **4d** (95.6−100.4°) are slightly smaller than the C−P−C bond angles of the free ligand **3** (96.8−103.5°). This suggests that the tridentate coordination of **3** to Zn^{II} induces no significant strain on the ligand independent of the coordinating anion. The natural bite of the ligand seems to be ideally tailored to the tris-chelating coordination of Zn^{II}. The already mentioned N−C−C−C torsion angles of **4a** and **4d** (Table 1) vary a bit more than those observed for **3**. This small deviation from coplanarity can be interpreted as being caused by weak interactions of the coordinating anion with the *p*-tolyl substituents.

Conclusion

We have synthesised the new *p*-tolyl-substituted tris(imidazolyl)phosphane ligand $Pim^{Me,pTol}$ (**3**) and prepared a variety of stable Zn^{II} complexes. $Pim^{Me,pTol}$ (**3**) is the first tris(imidazolyl)phosphane ligand with a hydrophobic cavity formed by three aryl substituents. The geometry of its zinc complexes (bond lengths, angles, bite of the ligand) is similar to the geometry of the tris(pyrazolyl)borate zinc complexes. A comparison of the X-ray structure analyses of the free ligand $Pim^{Me,pTol}$ (**3**) and the two complexes $[Pim^{Me,pTol}ZnCl]_2ZnCl_4$ (**4a**) and $[Pim^{Me,pTol}ZnNO_3]NO_3$ (**4d**) reveals that the tris(imidazolyl)phosphane ligand hardly changes its bond angles upon metal coordination. The natural bite angle of the ligand is obviously ideally suited for zinc ion complexation. The orientation of the *p*-tolyl groups in the Zn^{II} complex **4d** shows that the hydrophobic cavity can adjust to the nonspherical shape of the nitrate ligand. The cavity seems deep and wide enough to allow access of an additional small molecule. This aspect is probably important to the mimicry of carbonic anhydrase activity. We think that the $Pim^{Me,pTol}$ ligand **3** is more suitable for reaction in protic solvents than the $Tp^{R,R'}$ ligands with their B−N bonds that are inherently sensitive to hydrolysis.

Experimental Section

General Remarks: The compounds 5-tolyl-4-tosyloxazoline[12] and tris[2-(1-methyl-4-tolylimidazolyl)phosphane[10b] **3** were synthesised according to the literature procedures for analogous systems. Ethanol was purified and degassed by standard procedures. All other solvents and reagents were used without further purification. ^{1}H NMR spectra, ^{31}P NMR spectra and ^{13}C NMR spectra were recorded on a Bruker DRX 200 spectrometer, the 2D NMR spectra were recorded on a Bruker DRX 500 spectrometer. The chemical shifts (δ) are reported in ppm with the solvent signal as reference. The EI-mass spectra were recorded on a double focussing mass spectrometer, model 311 A Varian MAT, ionisation energy 70 eV. The FAB mass spectra were recorded on a mass spectrometer Finnigan, Model MAT 8200, with an NBA matrix.

5-Tolyl-4-tosyloxazoline (1): Prepared according to a literature procedure[12] with tosylmethyl isocyanide (25.0 g, 128 mmol), tolylaldehyde (15.4 g, 128 mmol) and finely powdered sodium cyanide (0.4 g, 8 mmol) in 100 mL of dry ethanol. Yield: 38 g (90%) as a colourless crystalline solid. − ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, tolyl C*H*$_3$), 2.49 (s, 3 H, tosyl C*H*$_3$), 5.07 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 2 Hz, 1 H, oxazoline C^5 *H*), 6.05 (d, $^3J_{HH}$ = 6 Hz, 1 H, oxazoline C^4 *H*), 7.24 (s, 5 H, tosyl C_6H_4, oxazoline C^2 *H*), 7.42 (d, $^3J_{HH}$ = 8 Hz, 2 H, $C_6H_2H_2CH_3$), 7.88 (d, $^3J_{HH}$ = 8 Hz, 2 H, $C_6H_2H_2CH_3$).

1-Methyl-4-tolylimidazole, Im^{Me,pTol} (2): A suspension of 5-tolyl-4-tosyloxazoline (102 g, 310 mmol) in 250 mL of benzene was stirred under nitrogen in a 500 mL autoclave fitted with an inlet tube and a PTFE insert. The hole device was cooled to −78 °C. Then, dry methylamine (39.9 g, 1.28 mol) was condensed into the autoclave which was subsequently heated with stirring to 120 °C. After 20 h a red orange mixture was obtained and flash chromatography (ethyl acetate/dichloromethane, 4:1) afforded crude 1-methyl-4-tolylimidazole (15 g, 87 mmol; 28% relative to **1**) which was recrystallized from diethyl ether as colourless flakes. − ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H, $C_6H_4CH_3$), 3.74 (s, 3 H, NC*H*$_3$), 7.16 (d, $^4J_{HH}$ = 1 Hz, 1 H, imidazolyl C^5*H*), 7.22 (d, $^3J_{HH}$ = 8 Hz, 2 H, *m*-*H* of *p*-tolyl), 7.49 (s, 1 H, imidazolyl C^2*H*), 7.69 (d, $^3J_{HH}$ = 8 Hz, 2 H, *o*-*H* of *p*-tolyl). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.6 (s, $C_6H_4CH_3$), 33.9 (d, *J* = 3 Hz, N*C*H$_3$), 115.9 (s, imidazole *C*^{2} H), 125.1 (s, 2C, *p*-tolyl *C*$^{7,7'}$H), 129.7 (s, 2C, *p*-tolyl *C*$^{8,8'}$H), 131.9 (s, *p*-tolyl *C*), 136.7 (s, *p*-tolyl *C*), 138.8 (d, *J* = 2 Hz, imidazole *C*^{5}H), 142.8 (s, imidazole *C*^{4}). − MS (EI): *m*/*z* (%) = 172 (100) [M$^+$], 157 (16) [M$^+$ − CH_3], 130 (21) [M$^+$ − CH_3 − NCH], 103 (16) [$C_8H_7^+$], 77 (12%) [$C_6H_5^+$].

Tris[2-(1-methyl-4-tolylimidazolyl)]phosphane, Pim^{Me,pTol} (3): The procedure for Pim^{iPr,iPr} [10b] was modified by using THF as solvent instead of diethyl ether and replacing the THF with dichloromethane before adding the ammonia solution. Preparation of **3** from 1-methyl-4-tolylimidazole (15 g, 87 mmol), *n*-butyllithium (62 mL, 99 mmol, 1.6 M in hexane), freshly distilled PCl_3 (4.2 g, 30 mmol) and 150 mL of THF. Yield: 7.4 g (14 mmol; 45% rel. to PCl_3) of tris[2-(1-methyl-4-tolylimidazolyl)]phosphane as a colourless solid after recrystallization from dichloromethane/hexane. − ^{1}H NMR ($CDCl_3$): δ = 2.38 (s, 9 H, $C_6H_4CH_3$), 3.76 (s, 9 H, NC*H*$_3$), 7.18 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$), 7.38 (s, 3 H, imidazole C^5 *H*), 7.68 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 21.7 (s, $C_6H_4CH_3$), 35.2 (m, N*C*H$_3$), 121.0 (s, imidazole *C*^{2}P), 125.2 (s, 2C, *p*-tolyl *C*$^{7,7'}$H), 129.6 (s, 2C, *p*-tolyl *C*$^{8,8'}$H), 131.7 (s, *p*-tolyl *C*), 136.8 (s, *p*-tolyl *C*), 141.1 (d, *J* = 11 Hz, imidazole *C*^{5}H), 143.5 (d, *J* = 9 Hz, imidazole *C*^{4}). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = −57.9. − MS (EI): *m*/*z* (%) = 544 (13) [M$^+$], 372 (16) [P($N_2C_{11}H_{11}$)$_2^+$ − H], 359 (76) [P($N_2C_{11}H_{11}$)$_2^+$ − CH_2], 202 (20) [$PN_2C_{11}H_{11}^+$], 173 (52) [Im$^{Me,pTol+}$ + H], 130 (30) [Im$^{Me,pTol+}$ − CH_3 − NCH].

Bis[chloro{tris[2-(1-methyl-4-tolylimidazolyl)]phosphane}zinc] Tetrachlorozincate, [Pim^{Me,pTol}ZnCl]$_2$ZnCl$_4$ (4a): A stirred solution of Pim^{Me,pTol} (546 mg, 1.00 mmol) in 40 mL of THF was treated with $ZnCl_2$ (126 mg, 0.925 mmol) in THF. The reaction mixture was heated under reflux for 30 min then stirred for an additional 12 h at 25 °C. The complex precipitated as a colourless powder, which was collected by filtration and washed with 30 mL of THF. Drying under vacuum afforded **4a** (0.37 g, 0.25 mmol; 82% rel. to $ZnCl_2$). − ^{1}H NMR (CD_3NO_2): δ = 2.37 (s, 9 H, *p*-tolC*H*$_3$), 4.12 (s, 9 H, NC*H*$_3$), 7.25 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$), 7.53 (d, $^4J_{PH}$ = 4 Hz, 3 H, imidazolyl C^5*H*), 7.61 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$). − ^{31}P NMR (CD_3NO_2): δ = −113.7. − MS (FAB): *m*/*z* (%) = 643 (83) [Pim^{Me,pTol}ZnCl]$^+$, 472 (14) [P($N_2C_{11}H_{11}$)$_2$ZnCl]$^+$, 438 (5) [P($N_2C_{11}H_{11}$)$_2$Zn]$^+$, 373 (6) [P($N_2C_{11}H_{11}$)$_2^+$], 202 (3) [$PN_2C_{11}H_{11}^+$] 77 (36) [$C_6H_5^+$].

Bromo{tris[2-(1-methyl-4-tolylimidazolyl)]phosphane}zinc Bromide, [Pim^{Me,pTol}ZnBr]Br (4b): This compound was prepared according to the procedure described for [Pim^{Me,pTol}ZnCl]$_2$ZnCl$_4$ (**4a**) with **3** (273 mg, 0.501 mmol) and $ZnBr_2$ (113 mg, 0.502 mmol). Yield: 0.31 g (80%) of **4b** as a colourless powder. − ^{1}H NMR (CD_3NO_2): δ = 2.38 (s, 9 H, *p*-tolC*H*$_3$), 4.22 (s, 9 H, NC*H*$_3$), 7.24 (d, $^3J_{HH}$ = 7 Hz, 6 H, $C_6H_2H_2CH_3$), 7.49 (d, $^4J_{PH}$ = 4 Hz, 3 H, imidazolyl C^5 *H*), 7.55 (d, $^3J_{HH}$ = 7 Hz, 6 H, $C_6H_2H_2CH_3$). − ^{31}P{^{1}H} NMR (CD_3NO_2): δ = −118.2. − MS (FAB): *m*/*z* (%) = 689 (25) [Pim^{Me,pTol}ZnBr]$^+$, 518 (5) [P($N_2C_{11}H_{11}$)$_2$ZnBr]$^+$, 438 (3) [P($N_2C_{11}H_{11}$)$_2$Zn]$^+$.

Iodo{tris[2-(1-methyl-4-tolylimidazolyl)]phosphane}zinc Iodide, [Pim^{Me,pTol}ZnI]I (4c): This compound was prepared according to the procedure described for [Pim^{Me,pTol}ZnCl]$_2$ZnCl$_4$ (**4a**) with **3** (273 mg, 0.501 mmol), ZnI_2 (159 mg, 0.498 mmol) and ethanol as solvent. Yield: 0.36 g (84%) of **4c** as a colourless powder. − ^{1}H NMR (CD_3NO_2): δ = 2.37 (s, 9 H, *p*-tolC*H*$_3$), 4.23 (s, 9 H, NC*H*$_3$), 7.24 (d, $^3J_{HH}$ = 7 Hz, 6 H, $C_6H_2H_2CH_3$), 7.46 (d, $^4J_{PH}$ = 5 Hz, 3 H, imidazolyl C^5*H*), 7.50 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$). − ^{31}P{^{1}H} NMR (CD_3NO_2): δ = −119.4. − MS (FAB): *m*/*z* (%) = 735 (100) [Pim^{Me,pTol}ZnI]$^+$, 564 (18) [P($N_2C_{11}H_{11}$)$_2$ZnI]$^+$, 438 (23) [P($N_2C_{11}H_{11}$)$_2$Zn]$^+$, 373 (26) [P($N_2C_{11}H_{11}$)$_2^+$].

Nitrato{tris[2-(1-methyl-4-tolylimidazolyl)]phosphane}zinc Nitrate, [Pim^{Me,pTol}ZnNO$_3$]NO$_3$ (4d): This compound was prepared according to the procedure described for [Pim^{Me,pTol}ZnCl]$_2$ZnCl$_4$ (**4a**) with $Zn(NO_3)_2{\cdot}6H_2O$ (298 mg, 1.00 mmol). Yield: 0.67 g (92%) of **4d** as colourless powder. − ^{1}H NMR (CD_3CN): δ = 2.40 (s, 9 H, *p*-tolC*H*$_3$), 4.10 (s, 9 H, NC*H*$_3$), 7.30 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$), 7.48 (d, $^3J_{HH}$ = 8 Hz, 6 H, $C_6H_2H_2CH_3$), 7.56 (d, $^4J_{PH}$ = 4 Hz, 3 H, imidazolyl C^5*H*). − ^{31}P{^{1}H} NMR (CD_3CN): δ = −117.8. − MS (FAB): *m*/*z* (%) = 670 (100) [Pim^{Me,pTol}ZnNO$_3$]$^+$, 438 (18) [P($N_2C_{11}H_{11}$)$_2$Zn]$^+$, 373 (16) [P($N_2C_{11}H_{11}$)$_2^+$], 202 (11) [$PN_2C_{11}H_{11}^+$], 77 (94) [$C_6H_5^+$], 51 (69) [$C_4H_3^+$].

X-ray Crystallographic Study: For all compounds Pim^{Me,pTol} (**3**), [Pim^{Me,pTol}ZnCl]$_2$ZnCl$_4$ (**4a**), and [Pim^{Me,pTol}ZnNO$_3$]NO$_3$ (**4d**) data collection was carried out using a Bruker Smart CCD system. All data were corrected for absorption using SADABS.[20] The structures were solved using direct methods [SHELX-97[21] (**3**) and (**4a**), SIR-97[22] (**4d**)] and refined using least-squares methods (SHELX-97). Before the final refinement of **4d** the electron density of a strongly disordered nitromethane molecule was treated with PLATON[23] using the built-in SQUEEZE routine.[24] Crystal data for **3**, **4a** and **4d** are summarised in Table 2. Requests concerning the

Table 2. Crystallographic data for $Pim^{Me,pTol}$ (**3**), $[Pim^{Me,pTol}ZnCl]_2[ZnCl_4]\cdot 3CH_3NO_2$ (**4a**) and $[Pim^{Me,pTol}ZnNO_3]NO_3$ (**4d**)

	3	**4a**	**4d**
Crystal shape	rectangular rod	triclinic	triangular plates
Crystal colour	colourless	colourless	colourless
Crystal size (mm^3)	$1.2 \times 0.3 \times 0.1$	$0.45 \times 0.25 \times 0.2$	$0.4 \times 0.4 \times 0.08$
Empirical formula	$C_{33}H_{33}N_6P$	$C_{69}H_{75}Cl_6N_{15}O_6P_2Zn_3$	$C_{33}H_{33}N_8O_6PZn$
Formula weight	544.62	1681.19	734.01
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*Cc*	$P\bar{1}$	$P\bar{1}$
a (Å)	6.4913(3)	11.3536(2)	10.6721(6)
b (Å)	24.1876(12)	17.99740(10)	11.2203(6)
c (Å)	18.7098(10)	19.6392(2)	17.9169(10)
α (°)	90	94.1396(9)	106.3791(12)
β (°)	94.0140(10)	105.9953(5)	92.2410(11)
γ (°)	90	95.8169(9)	114.1669(11)
V ($Å^3$)	2930.4(3)	3816.66(8)	1848.47(18)
Z	4	2	2
d (calc, g/cm^3)	1.234	1.463	1.319
Type of diffractometer	Bruker Smart CCD	Bruker Smart CCD	Bruker Smart CCD
Radiation used (λ, Å)	Mo-K_α (0.71073)	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Monochromator	Graphite	Graphite	Graphite
Data-collecting mode	ω-scans	ω-scans	ω-scans
Linear absorption coefficient (mm^{-1})	0.127	1.247	0.760
Temperature (K)	173(2)	173(2)	173(2)
Max., min. transmission	0.949229, 0.456016	0.754681, 0.637147	0.846095, 0.727768
Total reflections	6746	30943	14790
Independent reflections	3341	20075	9666
Unique reflections [$I \geq 2\sigma(I)$]	2716	12210	5514
R(int)	0.1170	0.0338	0.0361
Scan range	$1.68 \leq \theta \leq 29.99°$	$1.49 \leq \theta \leq 30.44°$	$1.20 \leq \theta \leq 30.22°$
Index ranges	$-8 \leq h \leq 2$	$-11 \leq h \leq 15$	$-8 \leq h \leq 14$
	$-33 \leq k \leq 34$	$-25 \leq k \leq 24$	$-15 \leq k \leq 15$
	$-11 \leq l \leq 26$	$-27 \leq l \leq 22$	$-24 \leq l \leq 25$
F(000)	1152	1728	760
R,[a] R_w [$I > 2\sigma(I)$][b]	0.0599, 0.1495	0.0544, 0.1236	0.0549, 0.1062
R indices (all data)	0.0757, 0.1644	0.1074, 0.1474	0.1110, 0.1249
Maximum d/s	0.727	3.475	0.694
Maximum e-density ($e\cdot Å^{-3}$)	0.362	1.342	0.618
Minimum e-density ($e\cdot Å^{-3}$)	−0.541	−1.304	−0.372
Used reflections	3341	20075	9666
L.S. restraints	2	11	0
Refined parameters	367	921	448
Goodness-of-fit on F^2	1.068	1.015	0.954

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. – [b] $R_w = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^4)]^{1/2})$, $S = [\Sigma\, w(F_o^2 - F_c^2)^2]/(n - p)^{1/2})$, n = number of reflections, p = parameters used, w calc of (**3**): $w = 1/[\sigma^2(F_o^2) + (0.0966P)^2 + 0.0000P]$, w(calc) of (**4a**): $w = 1/[\sigma^2(F_o^2) + (0.0592P)^2 + 2.8419P]$, w(calc) of (**4d**): $w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$

X-ray crystal structure section should be addressed to one of the authors (Dr. Gerd Rheinwald).

Crystals of **3** with X-ray quality were obtained by evaporation of an acetone solution. The selected crystal was a colourless rectangular rod with dimensions of $1.2 \times 0.3 \times 0.1$ mm^3 and data collection proceeded at 173 K.

X-ray quality colourless triangular plates of **4a** were grown by diffusion of hexane into a nitromethane solution at 293 K. A crystal of dimensions $0.45 \times 0.25 \times 0.2$ mm^3 was selected and data collection proceeded at 173 K.

Colourless triclinic crystals of **4d** suitable for an X-ray study were also grown by diffusion of hexane into a nitromethane solution at 293 K. A crystal of dimensions $0.4 \times 0.4 \times 0.08$ mm^3 was selected and data collection proceeded at 173 K.

All crystals were prepared and handled under perfluoropolyalkyl ether (ABCR GmbH & Co KG, viscosity 1600 cSt.).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-137726 **(3)**, -137727 **(4a)** and -137728 **(4d)**. Copies of the data can be obtained free of change on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support for this work was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Dr. Peters for measuring the 2D HMBC NMR spectra and for helpful discussions.

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Received December 6, 1999
[I99444]