cleophilicity of the azide.[11] Thus, we prepared the iminophosphorane–phosphenium salts **19** and **20**[12] by treatment of **16** and **17** with trimethylsilyl trifluoromethanesulfonate. **19** and **20** exhibited characteristic ^{31}P NMR chemical shifts for cationic dicoordinated phosphorus species. **19**: 22.95 (d), 309.51 (d), J_{PP} = 87.2 Hz. **20**: 20.53 (d), 294.30 (d), J_{PP} = 80.5 Hz (Scheme VII). Thermolysis and UV photolysis of **19** and **20** led to oligomers featuring broad ^{31}P NMR signals at around 0 ppm.

In conclusion, it appears that intermolecular Staudinger reactions are favored compared to intramolecular ones. The only evidence for the formation of cyclodiphosphazene has been obtained with the bulky diisopropylamino groups on both phosphorus atoms. It is reasonable to think that such bulky substituents slow down the intramolecular process and thus allow the intramolecular reaction. These observations suggest that the use of small substituents at both phosphorus atoms could make the (phosphanylimino)azidophosphoranes interesting monomers for synthesis of polyphosphazenes. These results once more emphasize the difficulty of synthesizing cyclodiphosphazenes. The large-scale preparation of such compounds remains a challenge.

Registry No. 3, 90670-65-8; **5**, 135665-16-6; **6**, 135665-17-7; **7**, 135665-18-8; **8**, 135665-19-9; **9**, 117874-63-2; **10**, 135665-20-2; **11**, 96455-38-8; **12**, 135665-21-3; **16**, 135665-22-4; **17**, 135665-23-5; **18**, 135695-47-5; **19**, 135665-25-7; **20**, 135665-27-9; trichlorophosphine, 7719-12-2; (dimethylamino)dichlorophosphane, 683-85-2.

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A Mononuclear Zinc Hydroxide Complex Stabilized by a Highly Substituted Tris(pyrazolyl)hydroborato Ligand: Analogies with the Enzyme Carbonic Anhydrase

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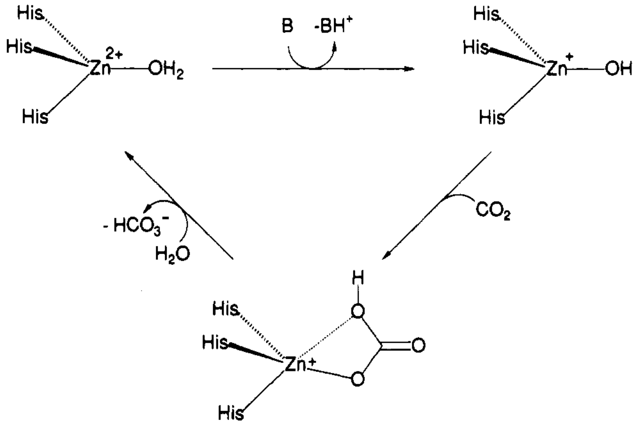
The enzyme carbonic anhydrase has a remarkably simple function, namely to catalyze the hydration of CO_2 to bicarbonate (eq 1). The catalytic site consists of a deceptively simple tetrahedral coordination environment in which a zinc center is bound to three histidine imidazole groups and a water molecule,

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \qquad (1)$$

$[His_3Zn–OH_2]^{2+}$ (His = histidine), and the initial stages of the catalytic cycle are considered to involve initial deprotonation of the coordinated water to give the active zinc hydroxide derivative $[His_3Zn–OH]^+$, followed by reaction with CO_2 to give a zinc bicarbonate derivative $[His_3Zn–OCO_2H]^+$ (Scheme I).[1] However, attempts to mimic structurally the zinc coordination environment in carbonic anhydrase by the synthesis of simple model compounds have met with only limited success,[2] while investigations to model the enzyme's function using other zinc complexes have generally been confined to ester hydrolysis studies.[3] At present there is no report of a fully characterized mononuclear tetrahedral $L_3Zn–OH$ complex, in spite of the facts that (i) basic salts are a common feature of the inorganic chemistry of zinc[4] and (ii) several hydroxide-bridged oligonuclear zinc complexes are known.[3d,5]

Scheme I. Simplified Catalytic Cycle for Hydration of CO_2



For studies designed to model structurally the active site of carbonic anhydrase, the tris(pyrazolyl)hydroborato ligand system, $\{HB(3,5\text{-}RR'pz)_3\}^-$ (RR'pz = substituted pyrazole), would appear to be an almost ideal choice for several reasons: (i) the three nitrogen atom donors of the $\{HB(3,5\text{-}RR'pz)_3\}^-$ ligand have the ability to bind to the zinc center in a manner analogous to that proposed for carbonic anhydrase, (ii) the sterically demanding tris(pyrazolyl)hydroborato derivatives, e.g. $\{HB(3\text{-}Bu^tpz)_3\}^-$, effectively restrict the maximum coordination of zinc to 4, and (iii) the uninegative nature of $\{HB(3,5\text{-}RR'pz)_3\}^-$ indicates that the tetrahedral hydroxide derivative $\{\eta^3\text{-}HB(3,5\text{-}RR'pz)_3\}ZnOH$ would be a neutral complex, which would thereby greatly simplify isolation procedures.[6] Indeed, our previous independent investigations of [tris(pyrazolyl)hydroborato]zinc chemistry have illustrated the validity of the aforementioned points,[5d,e,6c,d,7] and this paper reports the first result of our joint effort to synthesize and characterize a complex designed to model structurally the active site of the enzyme carbonic anhydrase.

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Table I. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

atom	*x*	*y*	*z*	U^a
Zn	0	0	0	32 (1)
O	0	0	−1970 (9)	55 (3)
N(11)	−1063 (4)	−532 (2)	2644 (5)	35 (2)
N(12)	−1239 (4)	−619 (2)	1197 (5)	36 (2)
C(11)	−1886 (5)	−943 (3)	3370 (7)	47 (3)
C(12)	−2621 (5)	−1311 (3)	2392 (9)	55 (3)
C(13)	−2194 (5)	−1097 (3)	1046 (8)	47 (3)
C(14)	−1942 (7)	−971 (3)	4956 (8)	72 (4)
C(15)	−2662 (5)	−1331 (3)	−391 (8)	55 (3)
C(16)	−3776 (7)	−1888 (3)	−210 (12)	131 (7)
C(17)	−2372 (5)	−1971 (5)	−1230 (6)	72 (3)
B	0	0	3185 (14)	40 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table II. Selected Bond Lengths (Å)

Zn–O	1.850 (8)	Zn–N(12)	2.052 (5)
Zn–N(12′)	2.052 (5)	Zn–N(12″)	2.052 (5)
N(11)–N(12)	1.380 (7)	N(11)–C(11)	1.329 (9)
N(11)–B	1.558 (7)	B–N(11′)	1.558 (7)
B–N(11″)	1.558 (7)	N(12)–C(13)	1.331 (9)
C(11)–C(12)	1.371 (10)	C(12)–C(13)	1.396 (11)

Table III. Selected Bond Angles (deg)

O–Zn–N(12)	123.2 (2)	O–Zn–N(12′)	123.2 (2)
N(12)–Zn–N(12′)	92.8 (2)	O–Zn–N(12″)	123.2 (2)
N(12)–Zn–N(12″)	92.8 (2)	N(12′)–Zn–N(12″)	92.8 (2)
N(12)–N(11)–C(11)	110.7 (5)	N(12)–N(11)–B	119.2 (6)
C(11)–N(11)–B	130.1 (6)	Zn–N(12)–N(11)	113.1 (4)
Zn–N(12)–C(13)	140.6 (5)	N(11)–N(12)–C(13)	106.3 (5)
N(11)–C(11)–C(12)	107.1 (6)	C(11)–C(12)–C(13)	107.0 (6)
N(12)–C(13)–C(12)	108.9 (6)	N(11)–B–N(11′)	109.9 (5)
N(11)–B–N(11″)	109.9 (5)	N(11′)–B–N(11″)	109.9 (5)

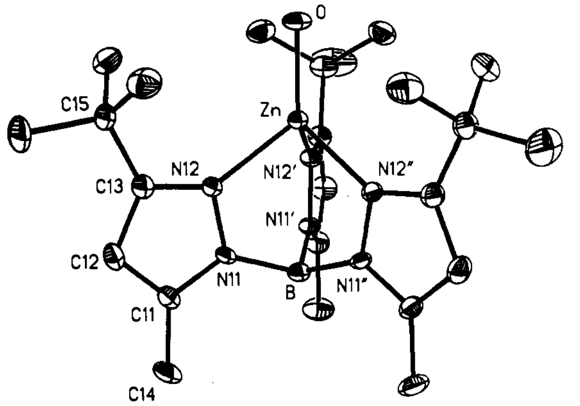
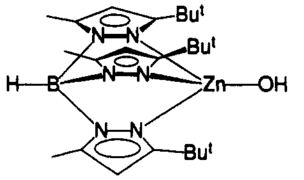


Figure 1. ORTEP diagram of $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH. Selected bond distances (Å) and angles (deg): Zn–O = 1.850 (8), Zn–N(12) = 2.052 (5), N(11)–N(12) = 1.380 (7), B–N(11) = 1.558 (7); N(12)–Zn–O = 123.2 (2), N(12)–Zn–N(12′) = 92.8 (2), N(11)–B–N(11′) = 109.9 (5).

Our previous experience has shown that, in order to stabilize a four-coordinate complex of the type $\{\eta^3$-HB(3,5-RR′pz)$_3\}$ZnOH, care must be taken to prevent (i) the formation of complexes with coordination numbers greater than 4,[6] (ii) oligomerization by OH bridging,[5d] and (iii) hydrolysis of the ligand's B–N bonds by Zn–OH or Zn–OH$_2$ functions.[5e] Tetrahedral coordination at zinc and inhibition of oligomerization are readily achieved by bulky substituents, e.g. *tert*-butyl, at the 3-position of the pyrazolyl ring.[5e,7] Similarly a protective pocket around the boron atom is provided by alkyl substitution at the 5-position of the pyrazolyl ring. A variety of tris(pyrazolyl)hydroborato ligands with appropriate substitution patterns have recently been prepared.[6c–e,8] Of these, we chose the 3-*tert*-butyl-5-methylpyrazolyl-substituted derivative {HB(3-Bu^t-5-Mepz)$_3$}K[8] for the synthesis of the target complex $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH



Results and Discussion

The reaction between equimolar amounts of Zn(ClO$_4$)$_2$·6H$_2$O, {HB(3-Bu^t-5-Mepz)$_3$}K, and KOH in methanol results in the formation of a precipitate of KClO$_4$ and a solution from which the desired complex $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH can be isolated in 65% yield:

$$\mathrm{Zn(ClO_4)_2} + \{\mathrm{HB(3\text{-}Bu^t\text{-}5\text{-}Mepz)_3}\}\mathrm{K} + \mathrm{KOH} \rightarrow \{\eta^3\text{-}\mathrm{HB(3\text{-}Bu^t\text{-}5\text{-}Mepz)_3}\}\mathrm{ZnOH} + 2\mathrm{KClO_4} \quad (2)$$

The hydroxide derivative $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH must be isolated immediately from the reaction mixture, otherwise significant decomposition is observed. While the fate of the zinc after decomposition remains unclear, the major organic decomposition product is 3-*tert*-butyl-5-methylpyrazole.[9] $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH was characterized both by spectroscopy (see the Experimental Section) and also by an X-ray crystal structure determination. Atomic coordinates and thermal parameters are listed in Table I, and selected bond distances and angles are listed in Tables II and III. The structure consists of discrete monomeric $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH units which possess a crystallographically imposed 3-fold rotation axis, as shown in Figure 1. The 3-fold symmetry implies a 3-fold disorder of the hydrogen atom of the OH group which, therefore, could not be located. The coordination environment about the zinc center in $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH is trigonally distorted tetrahedral, as evidenced by the three small N–Zn–N [92.8 (2)°] bond angles, typical for [tris(pyrazolyl)hydroborato]zinc complexes,[5e,7] and three accordingly large N–Zn–O [123.2 (2)°] bond angles. The remainder of the tris(pyrazolyl)hydroborato ligand has normal bond lengths and angles.[6] The Zn–O bond length [1.850 (8) Å] may be compared with those of some other zinc hydroxy complexes, $[\{\eta^2$-H$_2$B(3-Bu^{t}pz)$_2\}$Zn(μ-OH)]$_3$ [Zn–O = 1.89–1.99 Å],[5d] [(Bu^{t}pz)$_3$Zn(μ-OH)Zn(Bu^t-pz)$_3$](ClO$_4$)$_3$ [Zn–O = 1.901 (11), 1.914 (12) Å],[5e] and [((12)ane-N$_3$)Zn(OH)ClO$_4$]$_3$ [Zn–O = 1.944 (5) Å].[3d] Thus, although there is not a large variation of these bond lengths [1.85–1.99 Å] with the coordination number of zinc or the charge of the complex, the Zn–OH bond length is noticeably shorter in $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH than in the other complexes in which the hydroxy group bridges two zinc centers.

The coordination environment of $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH also compares reasonably well with a theoretical calculation for the active site of carbonic anhydrase, with bond lengths and angles of Zn–O = 1.96 Å, Zn–N = 2.10 Å, and O–Zn–N = 117.6°.[10a] However, the Zn–OH bond length is significantly shorter in $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH [1.850 (8) Å] than observed in the most recent structure determination (at 2.0-Å resolution) for the enzyme human erythrocytic anhydrase II, with bond lengths and angles of Zn–O = 2.1 Å, Zn–N = 1.9–2.1 Å, O–Zn–N = 108–114°, and N–Zn–N = 107–114°,[11] most probably as a consequence of the hydrogen-bonding network that exists for the latter.

The discussions of the structure and function of carbonic anhydrase have led to the suggestion that whereas the [enzyme–Zn–OH] complex is close to tetrahedral, the intermediate [en-

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Table IV. Crystal and Intensity Collection Data

formula	$C_{24}H_{41}N_6BOZn$	Z	3
fw	505.8	space group	$R3m$ (No. 160)
lattice	rhombohedral	radiation (λ, Å)	Mo Kα (0.71073)
cell consts	a = 15.995 (2) Å		
	b = 15.995 (2) Å	ρ_{calcd}	1.21 g cm^{-3}
	c = 9.391 (2) Å	μ(Mo Kα)	9.4 cm^{-1}
	α = 90.0°	goodness of fit	1.073
	β = 90.0°	R	0.0385
	γ = 120.0°	R_w[a]	0.0369
	V = 2080.5 (7) Å^3		

[a] Weighting scheme: $w = [\sigma^2(F) + 0.0002F^2]^{-1}$

zyme–Zn–OCO_3H] complex has a distorted 5-fold coordination (see Scheme I).[10] For both these geometries we have now found small-molecule equivalents in the form of [tris(pyrazolyl)hydroborato]zinc complexes, namely the hydroxide {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH with pseudotetrahedral coordination and the nitrate {η^3-HB(3-Phpz)$_3$}Zn(η^2-NO_3) with distorted 5-fold coordination.[5c] The new hydroxide complex {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH also seems to be promising with respect to the mechanism of carbonic anhydrase activity. Thus, we have observed that solutions of {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH do indeed reversibly absorb CO_2, giving a compound that shows two absorptions at 1675 and 1302 cm^{-1}, which may be assigned to the bicarbonate complex {η^3-HB(3-Bu^t-5-Mepz)$_3$}Zn(OCO_2H).[12] The bicarbonate complex undergoes subsequent reaction to give the bridging carbonate complex [{η^3-HB(3-Bu^t-5-Mepz)$_3$}Zn]$_2$(μ_2-OC(O)O),[13] in a manner analogous to that observed for the reaction of the dinuclear copper hydroxide complex [{η^3-HB(3,5-Pr$^i_2$pz)$_3$}Cu(μ-OH)]$_2$ to give [{η^3-HB(3,5-Pr$^i_2$pz)$_3$}Cu]$_2$(μ_3-CO_3)].[14]

Experimental Section

General Considerations. NMR spectra were recorded on a Bruker AC 200 FL spectrometer, and IR spectra were recorded as Nujol mulls on a Bruker IFS 25 spectrophotometer. Details of the preparation of {HB(3-Bu^t-5-Mepz)$_3$}K will be published elsewhere.[15]

Preparation of {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH. $Zn(ClO_4)_2 \cdot 6H_2O$ (205 mg, 0.55 mmol) was added to a solution of {HB(3-Bu^t-5-Mepz)$_3$}K (250 mg, 0.55 mmol) in methanol (40 mL). After 15 min, a solution of KOH (31 mg, 0.55 mmol) in methanol (10 mL) was added, and the mixture was stirred for 1 h at room temperature. The solution was filtered to remove the precipitate of $KClO_4$, and the filtrate was concentrated in vacuo at room temperature until {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH began to crystallize. Crystallization was completed by cooling to −20 °C for 24 h. The colorless crystals of analytically pure {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH (180 mg, 65%) were collected and dried under vacuum. IR (Nujol mull, cm^{-1}): ν_{OH} = 3676 (w), ν_{BH} = 2543 (m), 2521 (w). ^1H NMR (C_6D_6): δ 5.64 (s, 3 H, 3 CH), 2.10 (s, 9 H, 3 CH_3), 1.54 (s, 27 H, 3 C_4H_9), −0.07 (s, 1 H, Zn–OH).[16] ^{13}C NMR ($CDCl_3$): δ 162.8 (3 C, 3 pyrazole C=N), 143.9 (3 C, 3 pyrazole C=N), 102.3 (3 C, 3 pyrazole CH), 31.5 (3 C, 3 $C(CH_3)_3$), 30.3 (9 C, 3 $C(CH_3)_3$), 12.9 (3 C, 3 CH_3). Anal. Calcd for $C_{24}H_{41}BN_6OZn$: C, 56.99; H, 8.17; N, 16.62. Found: C, 56.70; H, 8.10; N, 16.42.

X-ray Structure Determination of {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH. Crystal data and data collection and refinement parameters are summarized in Table IV. A single crystal of {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected by using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å). Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects. The structure was solved by using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[17] Systematic absences were consistent with the space groups $R3$, $R\bar{3}$, $R32$, $R3m$, and $R\bar{3}m$, but consideration of the E value statistics, the axial photographs (a and b axes mirror symmetry), and the molecular symmetry strongly suggested the choice $R3m$ (No. 160). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions (d_{C-H} = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$). Block-diagonal least-squares refinement converged to R = 0.0385 (R_w = 0.0369). Inversion of configuration indicated the correct choice of enantiomorph. Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table I, and selected bond distances and angles are listed in Tables II and III.

Conclusion

The synthesis and structure determination of the zinc hydroxide complex {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH have provided the first mononuclear molecular analogue of the active center of the enzyme carbonic anhydrase, which also offers potential with respect to reactivity studies.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft (Grant Va 29/13), and the National Science Foundation Grant CHE-9007512). We thank two of the reviewers for valuable comments. G.P. is the recipient of an A. P. Sloan Research Fellowship (1991–1993) and a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996).

Supplementary Material Available: Tables SI–SVI, listing crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters for {η^3-HB(3-Bu^t-5-Mepz)$_3$}ZnOH (4 pages); a listing of calculated and observed structure factors (3 pages). Ordering information is given on any current masthead page.

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Palladium(I) π Complexes: An ESR Study of (Pentaphenylcyclopentadienyl)palladium Dibenzocyclooctatetraene

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Paramagnetic Pd π complexes are extremely rare. The most stable such complexes prepared to date are those of the type Cp*Pd(dien), where Cp* = η^5-C_5Ph_5 and dien = a cyclic diolefin such as 1,5-cyclooctadiene.[1] The Pd(I) compounds were generated by electrochemical reduction of the cationic Pd(II) precursors. Analogous Ni(I) complexes are also known.[2] Since knowledge of the half-filled orbital (SOMO) is of obvious relevance to the properties of this class of compound, we thought it would be useful to study a representative member by electron spin resonance (ESR) spectroscopy. The spin-$^5/_2$ ^{105}Pd nucleus is 22.2% in natural abundance, so that palladium nuclear hyperfine structure was expected in the ESR spectrum. Spin density information is carried by the metal nuclear hyperfine coupling tensor.

The pentaphenylcyclopentadienyl complex Cp*Pd(η^4-dbcot) (**1**), dbcot = dibenzocyclooctatetraene, was chosen for this purpose because of the high degree of stability imparted by the dbcot ligand.[1] An additional aspect of this choice was the conformational stability of the dbcot ligand. The aromatic rings have the effect

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