Table III. Bond Angles and Distances for **2**

A	B	C	angle, deg
Te(2)	Sn(1)	Te(3)	114.4 (0)
Te(2)	Sn(1)	Te(4)	113.7 (0)
Te(3)	Sn(1)	Te(4)	106.6 (0)
Te(4)	Sn(1)	Te(4)	95.0 (0)
Sn(1)	Te(4)	Sn(1)	85.0 (0)
C(6)	N(5)	C(7)	110.7 (8)
C(6)	N(5)	C(8)	108.4 (7)
C(6)	N(5)	C(9)	109.3 (7)
C(7)	N(5)	C(8)	109.0 (9)
C(7)	N(5)	C(9)	110.5 (9)
C(8)	N(5)	C(9)	108.8 (6)
C(11)	N(10)	C(12)	110.1 (6)
C(11)	N(10)	C(13)	109.8 (6)
C(11)	N(10)	C(14)	108.9 (6)
C(12)	N(10)	C(13)	109.5 (6)
C(12)	N(10)	C(14)	109.4 (6)
C(13)	N(10)	C(14)	109.2 (6)

A	B	dist, Å	A	B	dist, Å
Sn(1)	Te(2)	2.700 (2)	N(5)	C(8)	1.490 (10)
Sn(1)	Te(3)	2.689 (1)	N(5)	C(9)	1.509 (11)
Sn(1)	Te(4)	2.794 (1)	N(10)	C(11)	1.502 (9)
Sn(1)	Te(4)	2.804 (1)	N(10)	C(12)	1.502 (9)
N(5)	C(6)	1.495 (11)	N(10)	C(13)	1.506 (10)
N(5)	C(7)	1.481 (11)	N(10)	C(14)	1.499 (10)

We have determined the structure of $(Me_4N)_4Sn_2Te_6$ from single-crystal X-ray data. A sample was transferred anaerobically to the goniostat and cooled to −168 °C, at which temperature all data were collected. Table I shows the crystal data for **2**. The unit cell parameters were obtained from 44 reflections at −168 °C. The structure was solved by using direct methods and standard Fourier techniques, and all hydrogens were located and refined isotropically. All non-hydrogen atoms were refined anisotropically. The data were corrected for absorption by using an analytical technique. A final difference Fourier was featureless, the largest peak being 0.45 e·Å⁻³. The atomic coordinates and bond lengths and angles for non-hydrogen atoms are given in Tables II and III, respectively. A view of the $Sn_2Te_6^{4-}$ anion, including the

atom-labeling scheme and important distances and angles, is shown in Figure 4. Although the anion is required to have only a crystallographic center of inversion, it has effective D_{2h} symmetry. This geometry has been observed in many compounds including B_2H_6, $Rb_6In_2S_6$,[31] $Ge_2Se_6^{4-}$,[11] and $C_2S_2Cl_4$.[32]

Unlike that **1**, of the ^{119}Sn Mössbauer spectrum of **2** (Figure 5) shows a quadrupole interaction due to the lifting of rigorous T_d symmetry at the Sn site.

Summary and Conclusions

The extraction of Zintl phases to obtain tetrahedral main-group polyanions provides an alternative method of preparation to the well-known basic degradation of binary main-group chalcogenides in aqueous solution. Both methods, however, rely on protic solvents, so hydrolytically unstable species such as boron chalcogenides or silicon chalcogenides will be difficult to access by either method. For example, we recently showed that the extraction of certain K/Si/Te alloys with ethylenediamine gave the TeH⁻ anion instead of anionic silicon tellurides.[19]

By use of high-temperature reactions, Kreb's aqueous route, or the Zintl phase extractions used here, the preparation of a large number of structural analogues of the silicates containing heavier main-group elements should be possible.

(31) Deiseroth, H. J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *B31*, 953.
(32) Krebs, B.; Beyer, H. *Z. Anorg. Allg. Chem.* **1969**, *365*, 199.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Zn^{2+}-Catalyzed Decomposition of a Tris(imidazol-2-yl)phosphine. Crystal and Molecular Structure of [Bis(4,5-diisopropylimidazol-2-yl)phosphinic acid]dichlorozinc Hydrate

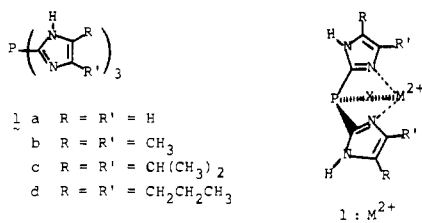R. G. BALL,* R. S. BROWN,* and J. L. COCHO

The reaction of an ethanolic solution of bis(4,5-diisopropylimidazol-2-yl)(imidazol-2-yl)phosphine with aqueous $ZnCl_2$ results in the formation of the title complex, $C_{18}H_{33}Cl_2N_4O_3PZn$, which was characterized by X-ray crystallography. The complex crystallizes in the space group $P2_1/c$ with unit cell dimensions of $a = 9.805$ (3) Å, $b = 26.202$ (7) Å, $c = 10.924$ (3) Å, $\beta = 111.79$ (2)°, and $Z = 4$. The structure refined routinely to a final R of 6.6%. The structural results indicate that the original phosphine has undergone oxidation and replacement of an imidazole by OH⁻, the latter process apparently being promoted by the presence of $ZnCl_2$. This result indicates that tris(imidazol-2-yl)phosphine–Zn^{2+} complexes, which are catalytically active models for the active site of carbonic anhydrase, suffer an apparent Zn^{2+}-promoted decomposition, which accounts for the observed loss of activity when they are allowed to stand in solution.

Introduction

Some time ago we initiated a project to synthesize tris(imidazol-2-yl)phosphines (**1**) and investigate their M^{2+} chelates (**1**:M^{2+}) as models for the active site in carbonic anhydrase.

During the course of these studies,[1–3] two general aspects of the chemistry became clear, first that the ligands themselves

(1) (a) Brown, R. S.; Curtis N. J.; Huguet, J. *J. Am. Chem. Soc.* **1981**, *103*, 6953. (b) Brown, R. S.; Huguet, J. *Ibid.* **1980**, *102*, 7571.

1
a R = R' = H
b R = R' = CH₃
c R = R' = CH(CH₃)₂
d R = R' = CH₂CH₂CH₃

were rather acid sensitive and second that the M^{2+} complexes deteriorated in solution after a few hours. The former feature necessitated the development of synthetic procedures to obtain 1 in which an easily hydrolyzed N-protecting group could be removed in the final step of the reaction without sacrificing the P–C bonds.[4,5] The sensitivity of the M^{2+} complexes was indicated by observations[1,2] that their catalytic activity toward facilitating the attainment of the $HCO_3^- \rightleftharpoons CO_2$ equilibrium deteriorated with the production of precipitates after a few hours of standing in buffered solutions (pH 6–7) at ambient temperature. Although each of the above complications can be circumvented under appropriate conditions, the peculiar decomposition of the chelates remained a serious enough matter that it prompted further investigation. Herein we report the results of a brief study of an unsymmetrical tris-(imidazol-2-yl)phosphine (2)[2] in terms of its decomposition
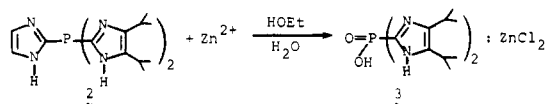
in solutions containing Zn^{2+} to yield a bis(imidazol-2-yl)-phosphinic acid–$ZnCl_2$ complex (3), whose structure we have determined by X-ray crystallography. We believe that 3 represents the first well-characterized example of a monomeric complex containing a chelating phosphinic acid.

Experimental Section

Ligand 2 was synthesized in 24.1% overall yield as described previously and fully characterized by spectral and analytical techniques.[2] Crystals of 3 were grown by slow diffusion of an EtOH solution of 2 into an aqueous solution of equimolar $ZnCl_2$. From the structure (vide infra) it is clear that during the course of crystallization (7 days) 2 had undergone decomposition to bis(4,5-diisopropyl-imidazol-2-yl)phosphinic acid with the expulsion of imidazole.

X-ray Data Collection and Reduction. Although crystals of 3 were generally of quite poor quality, one cut from a clump was adequate to use for collection of X-ray diffraction intensities. This crystal, with approximate dimensions 0.1 × 0.1 × 0.2 mm, was used for routine room-temperature ω–2θ data collection on an Enraf-Nonius CAD4 diffractometer using graphite crystal monochromated Mo Kα radiation. The scan range in ω was calculated to be $(0.7 + 0.35 \tan \theta)°$ with a 25% extension on either side for background determination.

The data were processed with standard computer programs.[6] Corrections for Lorentz, polarization, and background effects were applied, and those data with $I > 3\sigma(I)$ were considered observed and used for the solution and structure refinement. Crystallographic data are summarized in Table I.

Structure Solution and Refinement. Systematic absences determined the space group to be $P2_1/c$. The position for the Zn atom was determined from a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis. No attempt was made to include H atom contributions. Structure refinement converged with residuals of $R_1 = 0.066$ and $R_2 = 0.080$.

(2) Slebocka-Tilk, H.; Cocho, J. L.; Frackman, Z.; Brown, R. S. *J. Am. Chem. Soc.* **1984**, *106*, 2421.
(3) Brown, R. S.; Salmon, D.; Curtis, N. J.; Kusuma, S. *J. Am. Chem. Soc.* **1982**, *104*, 3188.
(4) Curtis, N. J.; Brown, R. S. *J. Org. Chem.* **1980**, *45*, 4038.
(5) Brown, R. S.; Ulan, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 2382.
(6) The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package (Frenz, B. A. "Computing in Crystallography"; Delft University Press: Delft, The Netherlands, 1978; pp 64–71) and several locally written or modified programs.

Table I. Summary of Crystallographic Data

formula	ZnCl₂PO₃N₄C₁₈H₃₃	a	9.805 (3) Å
fw	520.74	b	26.202 (7) Å
cryst dimens	0.1 × 0.1 × 0.2 mm	c	10.924 (3) Å
space group	monoclinic, $P2_1/c$	β	111.79 (2)°
D_c	1.327 g/cm³	V	2606.0 Å³
μ	12.55 cm⁻¹	Z	4

radiation	Mo Kα ($\lambda = 0.710\ 73$ Å)
monochromator	incident beam, graphite cryst
takeoff angle	3.05°
detector aperture	(2.00 + 0.50 tan θ) mm horizontal, 4.0 mm vertical
cryst-to-detector dist	205 mm
scan type	ω–2θ
scan rate	10.1–2.0°/min
scan width	$(0.70 + 0.35 \tan (\theta))°$
data collcn 2θ limit	55.0°
reflcns measd	5970 unique, 1674 with $I > 3\sigma(I)$
no. of params refined	197
$R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$	0.066
$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{0.5}$	0.080
GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{0.5}$	2.24
largest shift/esd, final cycle	0.4

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	$B,^a$ Å²
Zn	0.5204 (2)	0.10846 (6)	0.0890 (1)	4.78 (3)
Cl(1)	0.6779 (3)	0.0674 (1)	0.2648 (3)	5.76 (9)
Cl(2)	0.6033 (4)	0.1525 (2)	−0.0356 (4)	8.7 (1)
P	0.2473 (3)	0.0467 (1)	0.0318 (3)	3.59 (6)ᵇ
O(1)	0.3756 (7)	0.0528 (3)	−0.0084 (6)	3.9 (2)ᵇ
O(2)	0.0978 (7)	0.0350 (3)	−0.0613 (6)	3.9 (2)
O(3)	0.948 (1)	0.0568 (4)	0.185 (1)	9.9 (3)ᵇ
N(1)	0.2023 (9)	−0.0364 (3)	0.1748 (8)	3.8 (2)ᵇ
N(2)	0.4358 (9)	−0.0187 (3)	0.2225 (8)	3.8 (2)ᵇ
N(3)	0.3619 (9)	0.1361 (3)	0.1479 (8)	4.0 (2)ᵇ
N(4)	0.1422 (9)	0.1236 (3)	0.1598 (8)	4.5 (2)ᵇ
C(1)	0.295 (1)	−0.0047 (4)	0.149 (1)	4.0 (3)ᵇ
C(2)	0.283 (1)	−0.0733 (4)	0.268 (1)	4.4 (3)ᵇ
C(3)	0.430 (1)	−0.0607 (4)	0.300 (1)	4.1 (3)ᵇ
C(4)	0.212 (1)	−0.1153 (5)	0.316 (1)	6.8 (4)
C(5)	0.110 (1)	−0.0897 (7)	0.380 (1)	8.4 (5)
C(6)	0.125 (2)	−0.1496 (5)	0.201 (2)	9.5 (5)
C(7)	0.566 (1)	−0.0860 (5)	0.393 (1)	5.0 (3)
C(8)	0.610 (2)	−0.0622 (7)	0.530 (1)	9.3 (5)
C(9)	0.691 (1)	−0.0847 (6)	0.340 (1)	8.0 (4)
C(10)	0.250 (1)	0.1049 (4)	0.1203 (9)	3.7 (2)ᵇ
C(11)	0.330 (1)	0.1786 (4)	0.211 (1)	4.4 (3)ᵇ
C(12)	0.196 (1)	0.1708 (4)	0.217 (1)	4.6 (3)ᵇ
C(13)	0.428 (1)	0.2228 (5)	0.259 (1)	5.8 (4)
C(14)	0.432 (2)	0.2541 (5)	0.141 (2)	9.6 (6)
C(15)	0.582 (1)	0.2058 (6)	0.347 (2)	8.4 (5)
C(16)	0.099 (1)	0.2056 (6)	0.264 (1)	6.8 (4)
C(17)	−0.038 (2)	0.2232 (7)	0.143 (2)	12.6 (7)
C(18)	0.034 (2)	0.1781 (6)	0.350 (2)	11.6 (5)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$.
^{b} Indicates atoms were refined isotropically.

The highest peak in the final difference Fourier was 0.9(1) e Å⁻³ and is located near O(3) of the water molecule.

The final atomic positional and isotropic-equivalent thermal parameters are given in Table II. Tables of observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material.
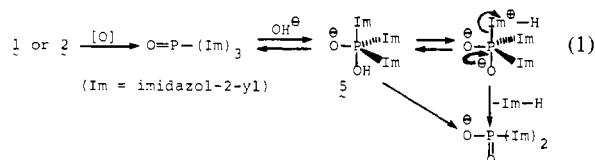
Results and Discussion

(a) Mechanistic Considerations. Crystals of 3 were obtained by slow diffusion of an ethanol solution of 2 into aqueous $ZnCl_2$ over a period of 1 week. From the structure (vide infra) it is clear that during this time the ligand suffered both oxidation

and spontaneous expulsion of the simple imidazole to yield bis(4,5-diisopropylimidazol-2-yl)phosphinic acid. In order to gauge the rapidity of this process under conditions akin to those that we have employed to investigate the catalytic activity of **2**:Zn^{2+} toward facilitating the attainment of $HCO_3^- \rightleftharpoons CO_2$ equilibration,[1,2] ^1H NMR analysis of an 80% ethanol/H_2O solution containing 2.2×10^{-2} M **2**, equimolar $ZnCl_2$ or Zn-$(ClO_4)_2$, and 2.5×10^{-2} M HEPES (*N*-(2-hydroxyethyl)-piperazine-*N'*-2-ethanesulfonic acid) was undertaken. Spectra were monitored over a 48-h period in the δ 9–6 region. Initially, the 4 and 5 H's of the simple imidazole appear as separate (but somewhat broadened) signals at δ 7.4 and 7.5,[2] respectively, indicating that they are fixed at different positions in the **2**:Zn^{2+} complex. No other peaks are seen in this region. However, after 48 h, a new signal centered at δ 7.7 develops, which is indicative of a 2-H resulting from an imidazole that had been cleaved from **2**. After 72 h, the low-field region exhibits singlets at δ 7.7 and 6.9 in a 1:2 ratio indicative of a free imidazole. Control experiments on solutions having the same composition either with no added $ZnCl_2$ or with Zn-$(ClO_4)_2$ (this being the source of Zn^{2+} in the catalytic studies[1,2]) indicate no such decomposition after a 48-h period. The latter solution does deteriorate with time to form an imidazole (as is evidenced by the appearance of a 2-H signal), but this requires a longer time than in the presence of $ZnCl_2$.

Conversion of phosphines with good leaving groups and phosphine oxides into their corresponding phosphinic acids has ample literature precedent.[7–9] In general, the departing alkyl group is the one having the lowest pK_a and is therefore more capable of supporting negative charge. This would explain why it is the simple imidazole rather than a diisopropyl-imidazole that is cleaved from **2**.

Although the detailed mechanistic aspects are unclear, we tentatively favor a process as in eq 1, akin to that proposed

$$1 \text{ or } 2 \xrightarrow{[O]} O=P-(Im)_3 \rightleftharpoons \ominus O-\underset{OH}{\overset{Im}{\underset{|}{P}}}Im \rightleftharpoons \cdots \qquad (1)$$

(Im = imidazol-2-yl)

by Newkome,[9] which involves nucleophilic attack of OH^- (or its kinetic equivalent) on the phosphine oxide (formed by spontaneous oxidation of **1** or **2**) to yield a bipyramidal phosphorane (**5**).

A few points are however worthy of consideration. Transformation of phosphine oxides to their corresponding phosphinic acids generally requires either fusion with $NaOH^{8e,f}$ or heating in concentrated alkaline solution[8a,c,d,9] unless a good leaving group (such as CF_3) can be displaced from the phosphorus, in which case the reaction proceeds under essentially neutral[8g] or mildly alkaline[7] conditions. Since neither of the imidazole units in **2** could be considered a good leaving group and since we have observed that decomposition of **1** or **2** in the absence of Zn^{2+} proceeds very slowly (except under highly acidic conditions[10]), the metal ion is in some way

Table III. Selected Bond Distances (Å)

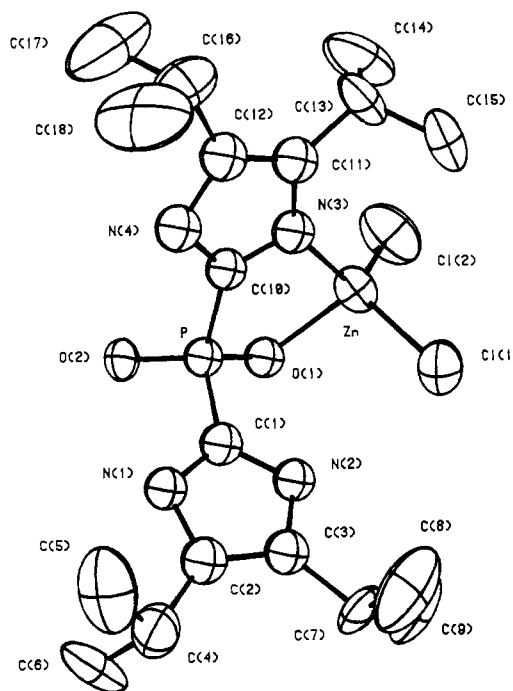| atom 1	atom 2	dist	atom 1	atom 2	dist
Zn	Cl(1)	2.243 (2)	N(1)	C(1)	1.340 (8)
Zn	Cl(2)	2.160 (3)	N(1)	C(2)	1.415 (9)
Zn	O(1)	2.037 (5)	N(2)	C(1)	1.360 (9)
Zn	N(3)	2.025 (6)	N(2)	C(3)	1.406 (9)
P	O(1)	1.487 (5)	N(3)	C(10)	1.315 (9)
P	O(2)	1.474 (5)	N(3)	C(11)	1.401 (9)
P	C(1)	1.797 (8)	N(4)	C(10)	1.368 (9)
P	C(10)	1.803 (8)	N(4)	C(12)	1.396 (9)

Figure 1. Perspective view of the molecule showing the atom-numbering scheme. Atoms are represented as 50% thermal ellipsoids.

catalyzing the process. This could involve a Lewis acid association of Zn^{2+} and imidazole to assist the latter's leaving and/or nucleophilic attack of a chelated $Zn^{2+}(OH^-)$ on the phosphorus, as in eq 2.

$$Im = (imidazol-2-yl) \qquad (2)$$
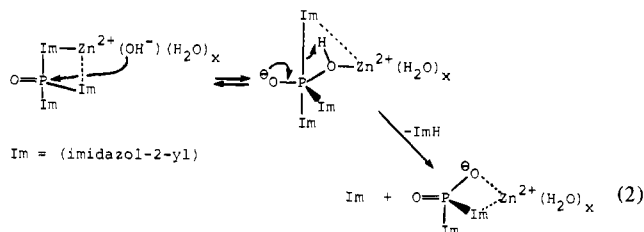
Both roles for M^{2+} have ample literature precedent, at least in the cleavage of carboxylic acid esters and amides and phosphate esters.[11–13] For example, assistance of the leaving group has been invoked to explain the M^{2+}-catalyzed hy-

(7) It has been reported that phenylbis(trifluoromethyl)phosphine undergoes reaction with OH^- and H_2O at 80 °C to yield fluoroform and phenylphosphonic acid: Beg, M. A. A.; Clark, H. C. *Can. J. Chem.* **1961**, *39*, 564.

(8) Phosphine oxides have been reported to undergo reaction with OH^- or OR^- to yield dialkylphosphinic acids: (a) Segall, Y.; Shirin, E.; Granoth, I. *Phosphorus Sulfur* **1980**, *8*, 243. (b) Allen, D. W.; Nutley, B. G.; Mellor, M. J. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1705. (c) Griffin, C. E.; Peller, R. P.; Peters, J. A. *J. Org. Chem.* **1965**, *30*, 91. (d) Martin, K. R.; Griffin, C. E. *J. Heterocycl. Chem.* **1966**, *3*, 92. (e) Horner, L.; Hoffmann, H.; Wippel, H. G. *Chem. Ber.* **1958**, *91*, 64. (f) Ezzell, B. R.; Freedman, L. D. *J. Org. Chem.* **1970**, *35*, 241. (g) Burg, A. B.; Sarkis, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 238. (h) Hoffmann, A. *Ibid.* **1930**, *52*, 2995.

(9) Newkome, G. R.; Hager, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 5567.

(10) We have observed that when $P(Im)_3$ ligands are heated in aqueous acid, cleavage of the P–C bonds occurs.[4] Undoubtedly the mechanism by which this occurs involves protonation of the imidazole, which facilitates its removal after attack by H_2O on P.

(11) Murakami, Y.; Sunamoto, J. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1827.

(12) Fife, T. H.; Przystas, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7297.

(13) Harrowfield, J. MacB.; Jones, D. R.; Lindoy, L. F.; Sargeson, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7733. (b) Buckingham, D. A.; Davis, C. E.; Foster, D. M.; Sargeson, A. M. *Ibid.* **1970**, *92*, 5571. (c) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *Ibid.* **1970**, *92*, 1726. (d) *Ibid.* **1974**, *96*, 1726. (e) Buckingham, D. A.; Keene, F. R.; *Ibid.* Sargeson, A. M. **1974**, *96*, 4981. (f) Groves, J. T.; Dias, R. M. *Ibid.* **1979**, *101*, 1033. (g) Brown, R. S.; Huguet, J.; Curtis, N. J. *Met. Ions Biol. Syst.* **1983**, *15*, 55–99.

Table IV. Selected Bond Angles (deg)

atom 1	atom 2	atom 3	angle
Cl(1)	Zn	Cl(2)	119.7 (1)
Cl(1)	Zn	O(1)	103.2 (2)
Cl(1)	Zn	N(3)	105.4 (2)
Cl(2)	Zn	O(1)	113.9 (2)
Cl(2)	Zn	N(3)	121.4 (2)
O(1)	Zn	N(3)	87.3 (2)
O(1)	P	O(2)	123.6 (3)
O(1)	P	C(1)	105.3 (3)
O(1)	P	C(10)	102.9 (3)
O(2)	P	C(1)	105.5 (3)
O(2)	P	C(10)	110.9 (3)
C(1)	P	C(10)	107.7 (3)
Zn	O(1)	P	115.2 (3)
Zn	N(3)	C(10)	112.4 (5)
Zn	N(3)	C(11)	140.9 (6)
C(10)	N(3)	C(11)	106.7 (7)
C(10)	N(4)	C(12)	104.4 (7)

drolysis of 8-quinolinyl phosphate[11] and 2-pyridylmethyl hydrogen phthalate,[12] while a nucleophilic role for $M^{2+}(OH^-)$ has often been proposed as an important pathway in metal-promoted hydrolyses.[12,13] However, insofar as we are aware, this case represents the first example whereby Zn^{2+} catalyzes the hydrolytic cleavage of a P–C bond.[14]

(14) (a) We have observed (Brown, R. S.; Huguet, J., unpublished results) that when an equimolar mixture of tris(4,5-diisopropyl-1-methyl-imidazol-2-yl)carbinol and ZnBr₂ is allowed to crystallize by controlled evaporation, crystals of [bis(4,5-diisopropyl-1-methylimidazol-2-yl)ketone]dibromozinc(II)[15] are deposited. Such a reaction requires a molecule of 4,5-diisopropyl-1-methylimidazole to be expelled from the carbinol, a process formally similar to the one reported in the present study. (b) It is noteworthy that the related silicon species behave similarly. For example (1-methylimidazol-2-yl)trimethylsilane hydrolyzes readily to produce 1-methylimidazole and trimethylsilanol. Mechanistically, the reaction involves OH⁻ attack on the N-protonated (imidazol-2-yl)trimethylsilane, the leaving group being the neutral zwitterion of N-protonated 1-methylimidazol-2-yl anion. Since OH⁻ does not attack the neutral (1-methylimidazol-2-yl)trimethylsilane, it is clear that in order for hydrolysis to occur the imidazole sp²-nitrogen lone pair must be associated with H⁺, a process formally akin to M²⁺ binding by the species reported herein: Brown, R. S.; Slebocka-Tilk, H.; Buschek, J. M.; Ulan, J. *J. Am. Chem. Soc.*, in press.
(15) For a crystal structure of [bis-(4,5-diisopropyl-1-methylimidazol-2-yl)ketone]dibromozinc(II), see: Read, R. J.; James, M. N. G. *Acta Crystallogr., Sect. B* **1980**, *B36*, 3100.

(b) Structure Description. Overall, the Zn^{2+} in the complex is coordinated approximately tetrahedrally by two Cl⁻'s and by N(3) of an imidazole and O(1) of the phosphinic acid as in Figure 1. From Table III, the Zn^{2+}–Cl distances (2.243 (2) and 2.160 (3) Å) and the Zn^{2+}–N(3) distance of 2.025 (6) Å compare favorably with those seen in [tris(4,5-diisopropylimidazol-2-yl)phosphine]dichlorozinc[16] (Zn–Cl = 2.170 (2) Å and Zn–N = 2.057 (2) Å, respectively). As is evidenced from the bond angles given in Table IV, the four-coordinate Zn^{2+} lies in a highly distorted tetrahedral environment, in which the angles vary from 87.3 (2)° (N(3)–Zn^{2+}–O(1)) to 121.4 (2)° (Cl(2)–Zn^{2+}–N(3)).

The bond lengths and angles in the two diisopropyl-imidazol-2-yl groups compare very well, as do the P–C distances, with those observed in a related tris structure.[16] The P–O distances of 1.487 (5) and 1.474 (5) Å agree nicely with the P–O distances in $Zn(OPPh_3)_2Cl_2$[17]. That the Zn–O distance of 2.037 (5) Å is somewhat longer than that in Zn-(OPPh₃)₂Cl₂ is not surprising considering the stereochemical constraints imposed by the nature of the chelating ligand.

From an examination of the intermolecular distances and a packing diagram, Figure 2 (see supplementary material), the only contacts of any significance are between O(3) of the water of crystallization and N(4) and O(2) (2.68 (1) and 2.71 (1) Å, respectively) of symmetry-related molecules, which may indicate the presence of a weak hydrogen-bonding network.

(16) Read, R. J.; James, M. N. G. *J. Am. Chem. Soc.* **1981**, *103*, 6947.
(17) Rose, M. P.; Lalancette; R. A.; Portenza, J. A.; Schugar, H. J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2409.

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Redox-Active Binuclear Complexes. Preparation, Oxidation, and Structure of Rh₂(Ph₂PCH₂PPh₂)₂(1,2-O₂C₆Cl₄)(CO)

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Treatment of [Ph₄As][Rh(1,2-O₂C₆Cl₄)(CO)₂] or a mixture of [Ph₄As][Rh(1,2-O₂C₆Cl₄)(CO)₂] and Rh₂(μ-Cl)₂(CO)₄ with bis(diphenylphosphino)methane (dpm) yields orange Rh₂(μ-dpm)₂(1,2-O₂C₆Cl₄)(CO). This compound crystallizes in the space group P1̄ (No. 2) with two molecules per unit cell of dimensions a = 11.126 (3) Å, b = 11.759 (3) Å, c = 20.065 (5) Å, α = 91.82 (2)°, β = 101.41 (2)°, γ = 92.23 (2)° at 140 K. Full-matrix least-squares refinement yielded R = 0.054. The structure consists of two distinct rhodium atoms: one five-coordinate and square pyramidal (with bonds to two oxygen atoms, two phosphorus atoms, and one out-of-plane rhodium atom) and the other four-coordinate and nearly planar (with bonds to two phosphorus atoms, one carbonyl carbon atom, and one rhodium atom). The Rh–Rh distance is 2.637 (1) Å. The two bridging bis(phosphine) ligands are arranged in an unusual fashion so that they are trans to one another at one rhodium, while they are cis to each other at the other rhodium. Rh₂(μ-dpm)₂(1,2-O₂C₆Cl₄)(CO) is reversibly oxidized electrochemically or chemically to a monocation, [Rh₂(μ-dpm)₂(1,2-O₂C₆Cl₄)(CO)]⁺, which has been characterized by electronic, infrared, and electron spin resonance spectra.

Introduction

There has been considerable development of the chemistry of binuclear rhodium complexes bridged by bis(diphenyl-phosphino)methane (dpm).[1-34] This work has shown that a

trans-Rh₂(μ-dpm)₂ unit is remarkably stable and can undergo a variety of reactions while retaining its structural integrity.

(1) Mague, J. T.; Mitchener, J. P. *Inorg. Chem.* **1969**, *8*, 119.