Inorg. Chem. **2001,** *40,* 6057−6060

Formation of a Novel Phenyldiphosphonic Acid Anion Dimer through Metal Assisted Hydrolysis of the P−N Bond

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Received June 12, 2001

Introduction

Polypyrazolyl borates $[HB(Pz)_3]^-$ and $[H_2B(Pz)_2]^-$ (Pz = pyrazolyl or substituted pyrazolyl) are among the most widely studied multidentate ligand systems.[1] This is due to three factors: (a) they are readily synthesized in very good yields by a one-step synthesis, (b) they have excellent binding properties toward a large range of transition and lanthanide metal ions,[2] and (c) these ligands can be easily modulated by varying the stereo-electronic properties of the substituents on the pyrazolyl group.[3] Because of these favorable properties pyrazolyl borates have found application as ligands in various research themes including organometallic[4] and bioinorganic chemistry.[5] In principle, the versatility of these polypyrazolyl borates can be matched by the corresponding phosphorus analogues $P(Pz)_3$, $(E)P(Pz)_3$, $RP(E)(Pz)_2$, or $R_2P(E)(Pz)$ [E = O, or S; R = alkyl or aryl]. However, in practice, the number of such examples is limited.[6a,b] One of the chief defects of the phosphorus based pyrazolyl ligands appears to be the hydrolytic sensitivity of the P−N bond particularly *after* interaction of the ligand with transition metal ions. Thus, tris(3,5-dimethyl pyrazolyl) phosphine oxide, $(3,5\text{-}Me_2Pz)_3P{=}O$, undergoes a P−N bond hydrolysis and is converted in situ into $[(3,5\text{-}Me_2Pz)_2PO_2]^-$ upon interaction with Cu(II) salts[6c] or a metal carbonyl.[6d] Recently we have observed an unusual desulfurization-cum-hydrolysis of $MeP(S)(3,5\text{-}Me_2Pz)_2$ upon interaction with $CuCl_2$.[7a] To probe if these reactions are general, we have prepared two different pyrazolyl ligands $PhP(O)(3,5\text{-}Me_2Pz)_2$, **1**, and $Ph_2P(O)(3,5\text{-}Me_2Pz)_2$, **2**, and studied their interaction with Pd(II) salts. In both of these cases we find that the interaction with the metal ion accelerates the P−N bond hydrolysis. These results are presented in this paper. We also report the X-ray crystal structure of $[Pd(3,5\text{-}Me_2Pz)_3Cl]^+[PhP(O)(OH)OP(O_2)Ph]^-$, **3**, which contains an anion formed from the condensation of the phenylphosphonic acid $PhP(O)(OH)_2$ formed in situ in the interaction of **1** and $PdCl_2$. This anion represents the first example of an anionic diphosphonic acid anhydride containing a P−C bond.

Experimental Section

The solvents were purified and dried according to standard procedures.[8] Diphenylphosphinic chloride, P,P-dichlorophenylphosphine oxide, and $PdCl_2{\cdot}2C_6H_5CN$ were acquired from Fluka, Switzerland, and used as such. Triethylamine (Qualigens, India) was dried over KOH and freshly distilled before use. The compound 3,5-dimethylpyrazole was prepared according to the literature procedure.[8]

Instrumentation. Infrared spectra were recorded as KBr pellets using a Bruker Vectra 22 FTIR spectrophotometer. ^1H and ^{31}P NMR spectra were recorded on a JEOL spectrometer operating at 400 and 60 MHz respectively. Mass spectra were recorded on a JEOL SX 102/ DA 6000 mass spectrometer using Xenon (6Kv, 10 mA) as the FAB gas. C, H, and N analyses were carried out at the Central Drug Research Institute's (Lucknow, India) regional instrumentation facility. All the preparative procedures described in the following were carried out under an inert gas atmosphere of dry N_2.

Synthesis of $PhP(O)(3,5\text{-}Me_2Pz)_2$, 1. P,P′-Dichlorophenylphosphine oxide (4.87 g, 24.9 mmol) was added dropwise through a syringe to a solution of 3,5-dimethylpyrazole (4.81 g, 50.0 mmol) and triethylamine (5.06 g, 50.0 mmol) in benzene at 10 °C. The reaction mixture was heated under reflux for 10 h. This was allowed to come to room temperature, filtered, and the filtrate stripped of the solvent in vacuo to afford a semisolid, which was dissolved in a mixture of CH_2Cl_2/*n*-hexane (1:1) and kept at 5 °C to afford **1** (yield: 7.00 g, 89%). Mp: 57 °C. IR (KBr): 3200(m), 1600(s), 1420(s), 1200(vs), 1150(w), 1090(m), 900(m), 810(w), 700(s) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.1$ (s, 6H, CH_3−), 2.3 (s, 6H, CH_3−), 5.9 (s, 2H, 4-*H* pyrazole), 7.8 (m, 5H, phenyl). ^{31}P NMR ($CDCl_3$): 13.7 (s). Mass(FAB): 315 [M^+]. Anal. Calcd for $C_{16}H_{19}N_4OP$ ($M_r = 314.32$): C, 61.13; H, 6.09; N, 17.82. Found: C, 61.01; H, 6.23; N, 17.91.

Synthesis of $Ph_2P(O)(3,5\text{-}Me_2Pz)$, 2. Diphenylphosphinic chloride (11.84 g, 50.0 mmol) dissolved in (20 mL) of dry benzene was added dropwise to a solution of 3,5-dimethyl pyrazole (4.81 g, 50.0 mmol) and triethylamine (5.06 g, 50.0 mmol) in benzene (100 mL) at 5 °C. The resulting mixture was heated under reflux for 10 h, cooled to room temperature, filtered, and the solvent removed from the filtrate under reduced pressure to afford a white crystalline solid. Recrystallization of this solid from hot CCl_4 gave colorless blocks of pure **2** (yield: 13.0

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g, 87%). Mp: 76 °C. IR (KBr) 3060(m), 2920(w), 2500(m), 1800(w), 1600(m), 1550(s), 1430(s), 1300(s), 1220(s), 1120(s), 1020(m), 800(m), 750(s) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.2$ (s, 3H, CH_3-), 2.5 (s, 3H, CH_3-), 5.9 (s, 1H, 4-H pyrazole), 7.4−7.8 (m, 10H, phenyl). ^{31}P NMR-($CDCl_3$): $\delta = 29.4$(s). Mass: 297[M$^+$]. Anal. Calcd for $C_{17}H_{17}N_2OP$ ($M_r = 296.30$): C, 68.90; H, 5.78; N, 9.45. Found: C, 68.81; H, 5.62; N, 9.40.

Reaction of PhP(O)(3,5-Me$_2$Pz)$_2$ 1 with PdCl$_2$(C$_6$H$_5$CN)$_2$. Ligand **1** (0.94 g, 2.9 mmol) was dissolved in 60 mL of dry dichloromethane and to it was added $PdCl_2(C_6H_5CN)_2$ (1.15 g, 2.9 mmol). The resulting mixture was stirred at 25 °C for 8 h. The solution was filtered, and the clear solution was evaporated to dryness under reduced pressure to yield a yellow powder. This was recrystallized from CH_2Cl_2/*n*-hexane (1:1) to afford a yellow crystalline material identified as $[Pd(3,5\text{-}Me_2Pz)_3Cl]^+$-$[PhP(O)(OH)OP(O)_2Ph]^{-1}$, **3** (yield: 1.03 g). Mp: 198 °C. IR (KBr) 3260(m), 2300(w), 1570(s), 1380(s), 1290(s), 1170(m), 1000(m), 980(m), 810(s), 750(w), 730(w), 720(m) cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 2.7$ (b, 18H, CH_3-), 5.8 (s, 3H, 4-*H* pyrazole), 8.2 (m, 10H, phenyl) 9.3 (b, 3H, N-*H*). ^{31}P NMR($CDCl_3$): 6.9(s).

Reaction of Ph$_2$P(O)(3,5-Me$_2$Pz), 2, with PdCl$_2$(C$_6$H$_5$CN)$_2$. The reaction of **2** (0.89 g, 3 mmol) with $PdCl_2(C_6H_5CN)_2$ (1.15 g, 2.9 mmol) was carried out in a 1:1 stoichiometry under similar conditions as described above. Removal of solvent afforded a residue. This was redissolved in CH_2Cl_2/*n*-hexane(1:1) and kept for crystallization. The product obtained was identified as $PdCl_2{\cdot}(3,5\text{-}Me_2Pz)_2$ **4** by X-ray crystallography.

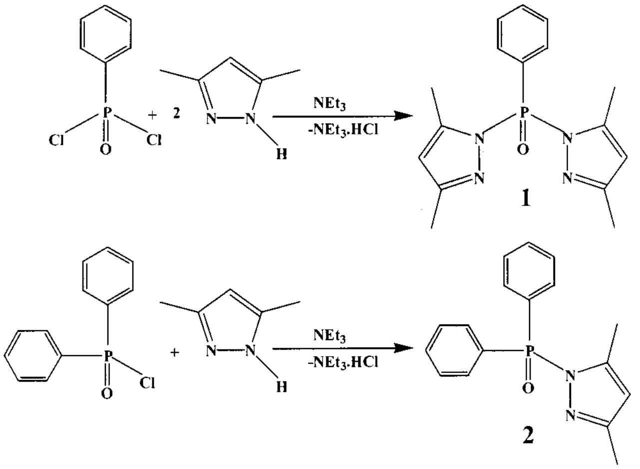
X-ray Diffraction Study of 2. Single crystals suitable for diffraction studies were grown by a slow evaporation of a solution of the compound in a mixture of CH_2Cl_2/ *n*-hexane. Yellow transparent blocks of **2** were obtained after a week's time. A single crystal of approximate dimension 0.30 mm × 0.20 mm × 0.15 mm was mounted for diffraction studies. The X-ray diffraction data were collected on a Siemens SMART3-circle diffractometer equipped with a CCD detector. The structure was solved by direct methods using the SHELX-90 program. The range of the angle **2** for data collection was from 1.78 to 28.34. A total of 19299 reflections were collected of which 7731 were unique with $R_{\mathrm{int}} = 0.0674$. The structure was solved by heavy atom method, completed by subsequent difference Fourier synthesis and refined on F^2 by full matrix least-squares procedures using SHELXTL[9] version 5.03.5. SADABS absorption correction was employed. The final goodness of fit was 1.030 and the largest differential peak and hole was 0.324 and $-0.395\ e^{-3}$. All hydrogens were fixed in their ideal positions using suitable riding models except for the N−H and O−H hydrogens, which were picked up from the Fourier map.

Results and Discussion

Synthetic Aspects. The ligands $PhP(O)(3,5\text{-}Me_2Pz)_2$, **1**, and $Ph_2P(O)(3,5\text{-}Me_2Pz)$, **2**, were prepared in nearly quantitative yields by the reaction of the corresponding phosphinic halides with 3,5-dimethylpyrazole in the presence of triethylamine as the hydrogen chloride scavenger (Scheme 1). Both **1** and **2** show sharp singlets in their ^{31}P{^{1}H}NMR at 13.7 and 29.4 ppm, respectively. These compounds also show prominent parent ion peaks in their FAB mass spectra. Another characteristic feature of these ligands is the strong P═O absorption at 1200 and 1120 cm^{-1}, respectively.

The interaction of the ligands **1** and **2** with $PdCl_2(C_6H_5CN)_2$ proceeds spontaneously and leads to *P−N hydrolyzed* products $[Pd(3,5\text{-}Me_2Pz)_3Cl]^+[PhP(O)(OH)OP(O_2)Ph]^-$, **3**, and $PdCl_2(3,5\text{-}Me_2Pz)_2$, **4**. Adventitious amounts of moisture seem to suffice for this hydrolysis. It was not possible to obtain any other products even when rigorous precautions were taken to exclude moisture from the reaction system. The products **3** and **4** were characterized crystallographically. The $PdCl_2(3,5\text{-}Me_2Pz)_2$ forms a dimer as a result of intermolecular hydrogen bonding between the Cl and the N−H protons of the coordinated pyrazole group (supplementary information). These hydrolysis reactions are reminiscent of the situations found by others and us previously.[7] As postulated by us previously it appears that in these ligands containing a *direct* P−N bond, upon metalation the electrophilicity of the phosphorus center in the ligands **1** and **2** is accentuated. This leads to the phosphorus center being readily susceptible to attack by nucleophilic reagents such as water. To prove this we have done an NMR experiment where the chemical shifts of the ligands did not change even in the presence of 3−4 equiv of water. However, upon the addition of palladium chloride to the ligands in the NMR tube, there was an immediate signal due to the formation of the hydrolyzed phosphinic acid $Ph_2P(O)(OH)$ or the phosphonic acid $PhP(O)(OH)_2$ or the diphosphonic acid anion $[PhP(O)(OH)OP(O_2)Ph]^-$ (Figure 1). Further evidence comes from the fact that the ligands where the pyrazolyl group is separated from the phosphorus by means of a spacer such as $Ph_2P(O)(OCH_2CH_2\text{-}3,5\text{-}Me_2Pz)$ are quite stable even upon interaction with transition metal ions.[10]

Scheme 1



X-ray Structure of [Pd(3,5-Me$_2$Pz)$_3$Cl]$^+$ [PhP(O)(OH)OP(O$_2$)Ph]$^-$, 3. Compound 3 crystallized in a monoclinic space group $P2_1/n$ with four molecules in the unit cell. Within an asymmetric unit there are two components, a monochloro palladium trispyrazole cation and a phenyldiphosphonic acid anion as shown in Figure 2. The metric parameters for this compound are also summarized in Figure 2; its structural refinement data are given in Table 1. The geometry around Pd(II) is square planar. Three free pyrazolyl ligands obtained from the in situ hydrolysis of the ligand coordinate to the metal ion. The fourth coordinating atom is a chloride ion. The Pd−Cl bond length is 2.2846(14) Å and the Pd−N(pyrazole) distance range from 1.999 to 2.023 Å. As shown in Figure 2 the hydrogen atoms attached to the nitrogens of the pyrazole ligands are involved in hydrogen bonding with the oxygen atoms of the diphosphonic acid moiety. The centroids of the cationic Pd moiety and anionic phenyl diphosphonic acid moiety are separated by 5.45 Å.

The most interesting feature of compound **3** is the diphosphonic acid anion. Although there are many examples of this structural motif involving condensed inorganic phosphates, the anion in **3** represents the first example of its type involving an organophosphorus compound. There is only one other example related to the anion in **3**, viz., 1,8-naphthahlene diphosphonic

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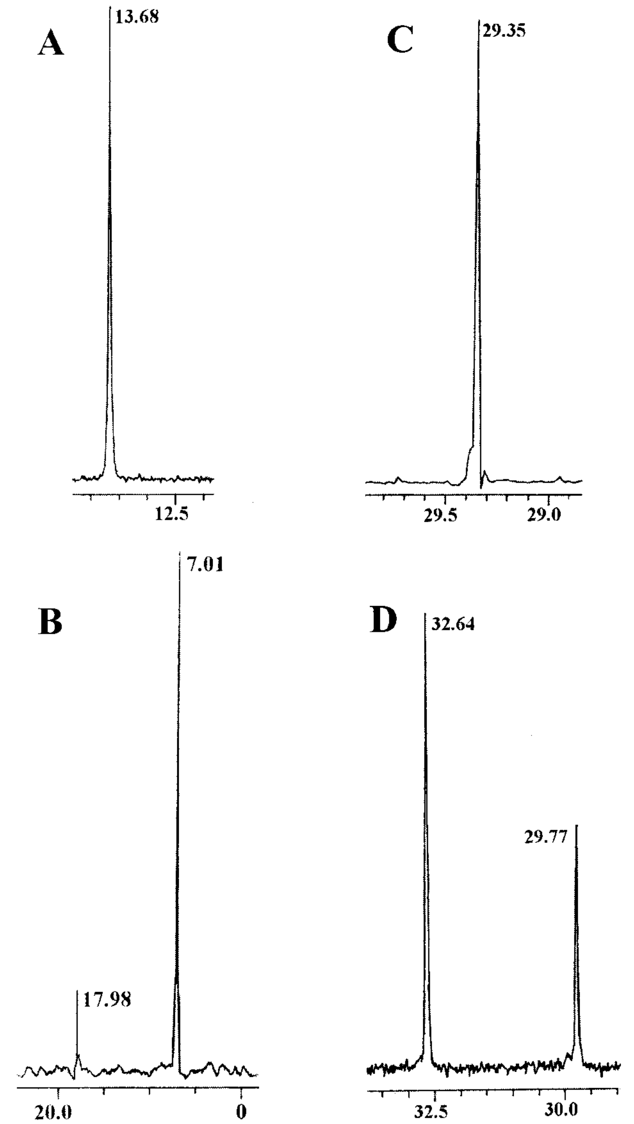

Figure 1. (A) $^{31}P\{^1H\}$ NMR spectrum of $PhP(O)(3,5\text{-}Me_2Pz)_2$. (B) $^{31}P\{^1H\}$ NMR spectrum of $PhP(O)(3,5\text{-}Me_2Pz)_2$ recorded immediately after the addition of $PdCl_2(C_6H_5CN)_2$. Note the disappearance of ligand peak. Peak at 7.01 corresponds to$[PhP(O)(OH)OP(O_2)Ph]^-$ $[Pd(3,5\text{-}Me_2Pz)_3Cl]^+$ while peak at 17.98 corresponds to $PhP(O)(OH)_2$. (C) $^{31}P\text{-}\{^1H\}$ NMR spectrum of $Ph_2P(O)(3,5\text{-}Me_2Pz)$. (D) $^{31}P\{^1H\}$ NMR spectrum of $Ph_2P(O)(3,5\text{-}Me_2Pz)$ recorded immediately after the addition of $PdCl_2(C_6H_5CN)_2$. The new peak at 32.64 corresponds to $Ph_2P(O)OH$.

acid anhydride.[11] The formation of the anion in **3** presumably occurs by the condensation of phenyl phosphonic acid generated insitu by the hydrolysis of **1**. Evidence for the formation of phenylphosphonic acid comes from $^{31}P\{^1H\}$ NMR data (vide supra). The geometry around each phosphorus center in the diphosphonic acid anion is tetrahedral. Each phosphorus is connected to three oxygen atoms and a phenyl substituent. Thus, P1A is attached to the $O2(P-O^-)$ with a bond distance of 1.528 Å. In contrast the P1−O1(P═O) distance is 1.468 Å. The latter is analogous to P═O distances found in the literature; thus, in $Ph_2P(O)NMe_2$ and $Ph_2P(O)(OH)$ the observed P═O distances are 1.47 and 1.45 Å, respectively.[12] The P1−O3 and the P2−O3 bridging distances (P−O−P) are 1.603 and 1.615 Å and

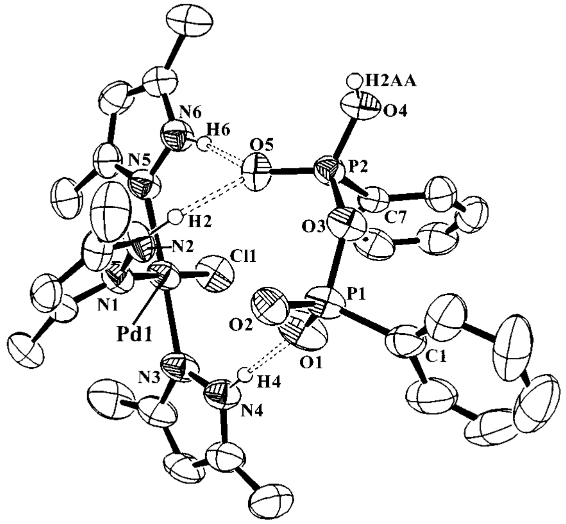

Figure 2. ORTEP plot of **3** (asymmetric unit) with thermal ellipsoids at 50% probability. All hydrogen atoms except those involved in hydrogen bonding are omitted for clarity. Important bond lengths (angstroms) and bond angles (degrees) are Pd(1)−Cl(1) 2.2846(14), Pd(1)−N(1) 2.023(4), Pd(1)−N(3) 1.999(4), Pd(1)−N(5) 2.021(4), N(2)−H(2) 0.870(4), N(4)−H(4) 0.87(6), N(6)−H(6) 0.82(5), O(1)···H(4) 1.81(6), O(5)···H(2) 1.932(3), O(5)···H(6) 1.92(5), N(6)−H(6)−O(5) 168(5), N(2)−H(2)−O(5) 165.4(3), N(4)−H(4)−O(1) 172(5), N(1)−Pd(1)−Cl(1) 178.26(12), N(3)−Pd(1)−Cl(1) 89.53(12), N(3)−Pd(1)−N(1) 89.9(2), N(3)−Pd(1)−N(5) 176.0(2), N(5)−Pd(1)−Cl(1) 88.57(11), and N(5)−Pd(1)−N(1) 92.1(2).

Table 1. Details of Data Collection and Structure Refinement for **3**

empirical formula	$C_{27}H_{35}Cl_1N_6O_5P_2Pd_1$
fw	727.42
crystal syst/space group	monoclinic/$P2_1/n$
a, Å	12.5566(5)
b, Å	15.8960(6)
c, Å	16.8390(6)
β, deg	101.351(1)
V, Å^3	3295.3(2)
Z	4
temp, K	213(2)
λ(Mo Kα), Å	0.710 73
D_{calcd}, g cm^{-3}	1.466
μ, mm^{-1}	0.785
R1^a	0.0534
wR2^b	0.1292

$^a R = R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b Rw = \{[\Sigma w(|F_o|^2 - |F_c|^2)^2]/[\Sigma w(|F_o|^2)^2]\}^{1/2}$.

represent the longest P−O distances found in this molecule. Interestingly the P2−O4(P−OH) is 1.488 Å and is considerably shorter than either the bridging P−O distance or the $P-O^-$ distance. The bridging P−O−P angle is 130.9°. The P−O−P angles in pyrophosphates range from 130° to 180°.[12] The most interesting feature of the diphosphonic acid dianion is the dimer formation between two such molecules by means of O−H···O hydrogen bonding (Figure 3). The hydrogen H2A attached to the oxygen (O4A-*H2A*) of the symmetry generated unit has a strong intermolecular interaction with the oxygen O2(P1-*O2*). Similarly the hydrogen H2AA(O4-*H2AA*) also interacts in an intermolecular manner with O2A(P1A-*O2A*) generating a cyclic 12-membered ring. The hydrogen bonding parameters are summarized in Figure 3 and are perfectly consistent with known O−H··· O interactions;[12] thus, the O(2)−O(4A) distance is 2.424 Å and the O2−H2A−O4A angle is 162°. The 12-membered

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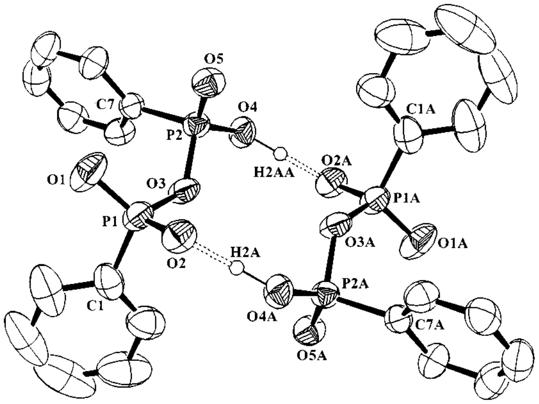

Figure 3. ORTEP plot of the 12-membered ring formed by the phenyl diphosphonic acid anion dimer linked through hydrogen bonding. Thermal ellipsoids at 50% probability. Important bond lengths (angstroms) and bond angles (degrees) are P(1)−C(1) 1.793(6), P(1)−O(1) 1.468(4), P(1)−O(2) 1.528(3), P(1)−O(3) 1.603(3), P(2)−C(7) 1.790(5), P(2)−O(3) 1.615(3), P(2)−O(4) 1.488(3), P(2)−O(5) 1.491(3), O(4)−H(2AA) 1.02(6), H(2AA)- - - -O(2A) 1.43(6), O(4)···O(2A) 2.424(5), C(1)−P(1)−O(1) 112.2(3), C(1)−P(1)−O(3) 101.5(2), C(1)−P(1)−O(2) 109.5(2), O(1)−P(1)−O(2) 114.4(2), O(1)−P(1)−O(3) 112.9(2), O(2)−P(1)−O(3) 105.4(2), C(7)−P(2)−O(3) 104.7(2), C(7)−P(2)−O(4) 107.8(2), C(7)−P(2)−O(5) 111.3(2), O(3)−P(2)−O(4) 105.2(2), O(3)−P(2)−O(5) 109.1(2), O(4)−P(2)−O(5) 117.8(2), P(1)−O(3)−P(2) 130.9(2), and O(4)−H(2AA)-O(2A) 162(5).

ring is puckered and the phosphorus atoms P(1), P(2), P(1A), and P(2A) form a single plane. The rest of the atoms in the ring are out of the plane; thus, O3, O4, and O2A are on one side of the plane while O3A, O2, and O4A lie on the other side. Interestingly the diphosphonic acid anion dimer interacts with the two cation subunits through N−H···O interactions involving the NH of the pyrazole ligand in the cation and the P═O units of the anion. Thus, P1−O1 is involved in hydrogen bonding with one pyrazolyl group N4-*H4* while P2−O5 is involved in hydrogen bonding with two pyrazolyl groups N6-*H6* and N2-*H2*.

In conclusion we describe the metal assisted hydrolysis of P−N bonds involving phosphorus pyrazolides PhP(O)(3,5-Me_2-Pz)$_2$, **1**, and $Ph_2P(O)(3,5\text{-}Me_2Pz)_2$, **2**. A novel feature of the interaction of **1** with $PdCl_2(C_6H_5CN)_2$ is the formation of an unusual diphosphonic acid anion.

Acknowledgment. We are thankful to Department of Science and Technology (India) for financial support. S.K. is thankful to the Council of scientific and Industrial Research (India) for a Senior Research Fellowship.

Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of **3**, two figures of **4** with metric parameters, and a DIAMOND view of the entire fragment of **3** within the unit cell. This material is available free of charge via the Internet at http://pubs.acs.org./

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