availability of excited states that respectively lead to angular (ligand field) and radial (charge transfer) reorganizations of the electronic density with respect to the ground state can justify, therefore, the observed photochemical properties of the Mo(V) dimers.

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## Two Polymorphs of the Diazaphosphole Oxide $C_6H_4(NH)_2P(O)Ph$

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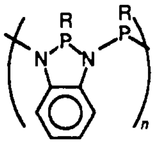
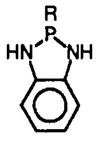
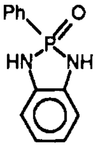
Our investigations of skeletally stabilized P(III) phosphazane oligomers/polymers (**1**)[1,2] have stimulated studies of P(III) and P(V) 1,3-dihydro-1,3,2-diazaphospholes, especially the *P*-phenyl derivatives **2** (R = Ph) and **3**. Pilgram and Korte[3] claimed the



**1**



**2**



**3**

preparation of **2** (R = $MeC_6H_4$) from the 1,2-$(NH_2)_2C_6H_4$/$MeC_6H_4P(OPh)_2$ reaction; however, the characterization was inconclusive. Even the oxide **3** has been only partially characterized.[4,5] We now wish to report recent studies of these systems and the discovery that **3** can be obtained in two polymorphic crystalline forms.

### Experimental Section

**Apparatus and Materials.** $^{31}P$ and $^1H$ NMR spectra were recorded with a JEOL FX-90Q spectrometer at 36.5 and 90.0 MHz, respectively. $^{31}P$ and $^1H$ NMR chemical shifts downfield from 85% $H_3PO_4$ (external) and $(CH_3)_4Si$ (internal) are reported as positive (+δ). IR spectra (4000–400 cm$^{-1}$) were obtained with a Beckman 4250 grating spectrometer. Mass spectra were obtained at 70 eV with a VG Analytical 7070 EQ-HF spectrometer. Elemental analyses were performed by Huffman Laboratories Inc., Wheatridge, CO. All manipulations were carried out by using standard glovebag techniques under dry $N_2$.[6]

1,2-$(NH_2)_2C_6H_4$ (Aldrich) was recrystallized from toluene. $Et_3N$ (Baker) was distilled from $CaH_2$. Toluene (over Na/Pb alloy) and $CH_2Cl_2$ (over $P_4O_{10}$) were distilled before use. $PhPCl_2$ (Strem Chemicals) was distilled from $CaH_2$. $PhP(O)Cl_2$ (Aldrich) was used as obtained. $PhP(OPh)_2$, prepared as described previously,[7] after vacuum distillation contained ca. 3% (m/m) $PhP(O)(OPh)_2$ (by $^{31}P$ NMR). $[C_6H_4N_2(PPh)_2]_2$ was obtained as described elsewhere.[1]

**Table I.** Crystal Data, Data Collection Parameters, and Refinement Details for $C_6H_4(NH)_2P(O)Ph$ (**3A** and **3B**)

| | **3A** | **3B** |
|---|---|---|
| formula | $C_{12}H_{11}N_2OP$ | $C_{12}H_{11}N_2OP$ |
| fw | 230.20 | 230.20 |
| space group | *Pnma* | *Cmca* |
| *a*, Å | 17.816 (4) | 7.679 (2) |
| *b*, Å | 7.578 (2) | 17.127 (3) |
| *c*, Å | 8.709 (2) | 17.210 (4) |
| V, Å$^3$ | 1175.9 (4) | 2263.3 (8) |
| *Z* | 4 | 8 |
| λ, Å | 1.54178 (Cu Kα) | 0.71069 (Mo Kα) |
| $d_{calc}$, g cm$^{-3}$ | 1.30 | 1.35 |
| *F*(000) | 480 | 960 |
| temp, °C | 22–24 | 22–24 |
| μ, cm$^{-1}$ | 19.1 | 2.15 |
| *R* | 0.036 | 0.039 |
| $R_w$ | 0.051 | 0.055 |

**Table II.** Positional (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for $C_6H_4(NH)_2P(O)Ph$ (**3A**)

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| P(1) | 4586 (1) | 2500 | 9233 (1) | 39 (1) |
| O(1) | 5342 (1) | 2500 | 9951 (2) | 47 (1) |
| N(1) | 4002 (1) | 4075 (3) | 9772 (2) | 45 (1) |
| C(1) | 4675 (2) | 2500 | 7202 (3) | 48 (1) |
| C(2) | 5373 (2) | 2500 | 6524 (4) | 77 (22) |
| C(3) | 5428 (3) | 2500 | 4928 (6) | 107 (2) |
| C(4) | 4794 (4) | 2500 | 4049 (5) | 107 (2) |
| C(5) | 4116 (3) | 2500 | 4706 (5) | 101 (2) |
| C(6) | 4043 (2) | 2500 | 6283 (4) | 71 (1) |
| C(7) | 3398 (1) | 3416 (3) | 10638 (2) | 45 (1) |
| C(8) | 2855 (1) | 4353 (4) | 11413 (3) | 60 (1) |
| C(9) | 2305 (1) | 3401 (4) | 12203 (3) | 72 (1) |

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

**Table III.** Positional (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for $C_6H_4(NH)_2P(O)Ph$ (**3B**)

| atom | *x* | *y* | *z* | $U^a$ |
|---|---|---|---|---|
| P(1) | 0 | 2078 (1) | 2042 (1) | 41 (7) |
| O(1) | 0 | 2338 (3) | 2865 (3) | 50 (2) |
| N(1) | 1550 (5) | 2428 (2) | 1472 (2) | 46 (2) |
| C(1) | 0 | 1037 (5) | 2000 (5) | 45 (3) |
| C(2) | 0 | 620 (6) | 2687 (6) | 71 (4) |
| C(3) | 0 | −200 (7) | 2648 (9) | 97 (6) |
| C(4) | 0 | −578 (7) | 1958 (9) | 97 (5) |
| C(5) | 0 | −168 (7) | 1280 (9) | 90 (5) |
| C(6) | 0 | 641 (5) | 1294 (5) | 63 (4) |
| C(7) | 908 (6) | 2943 (3) | 913 (3) | 40 (2) |
| C(8) | 1820 (8) | 3408 (4) | 399 (3) | 53 (2) |
| C(9) | 894 (8) | 3887 (4) | −97 (4) | 63 (2) |

[a] See footnote *a*, Table II.

**$C_6H_4(NH)_2P(O)Ph$ (3). Polymorph 3A.** 1,2-$(NH_2)_2C_6H_4$ (17 mmol) and $PhP(OPh)_2$ (17 mmol) were heated in vacuo at 120 °C. After 18 h, $^{31}P$ NMR spectral resonances occur at δ 157.8 ($PhP(OPh)_2$), 110.5 (**4**), 26.5 (**3**), and 12.8 ($PhP(O)(OPh)_2$) (mol % 69:16:10:5). Upon further heating, the resonance at δ 110.5 (**4**) decreased in intensity. Cooling to 25 °C precipitates **3** from the reaction mixture as **3A** (yield 1.4 g, 33% yield). Attempts to isolate **4** failed.

$PhP(O)Cl_2$ and 1,2-$(NH_2)_2C_6H_4$ were allowed to react in PhBr as described previously.[4] Recrystallization of the product from $CHCl_3$ gave **3A** (mp 278–279 °C; >85% yield, lit.[4] yield 100%). $^{31}P\{^1H\}$ NMR ($(CD_3)_2SO$): δ 25.5 (s). $^1H$ NMR: δ 9.09 (s). IR (KBr, cm$^{-1}$): 3182 (s, N—H), 1260 (s, P═O).[5] MS: *m*/*e* 320 ($M^+$, $C_{12}H_{11}N_2OP^+$). Anal. Calcd for $C_{12}H_{11}N_2OP$: C, 62.60; H, 4.82; N, 12.17; P, 13.46. Found: C, 62.50; H, 4.94. **3** is only slightly soluble in toluene and $CH_2Cl_2$ and soluble in $Me_2SO$.

**Polymorph 3B.** Crystallization of $[C_6H_4N_2(PPh)_2]_2$, prepared from the 1,2-$(NH_2)_2C_6H_4$/$PhPCl_2$ reaction in toluene,[1] from the toluene reaction solution yields trace quantities of **3** (<1% yield) as **3B** (mp 280–281 °C).

**X-ray Analyses.** Crystals of **3A** and **3B** were mounted on glass fibers and coated with epoxy resin. Cell parameters were determined on the

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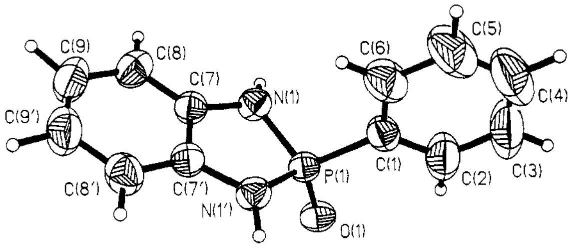

**Figure 1.** Structure of **3A** showing the numbering system used for both polymorphs. Thermal ellipsoids are shown at the 50% probability level. The structures of **3A** and **3B** are superimposable with an average deviation of 0.027 Å (maximum 0.056 Å for C(4); minimum 0.006 Å for C(7)).

basis of the least-squares refinement of the setting angles of 25 (**3A**) and 15 (**3B**) centered reflections. Crystal data are summarized in Table I. **3A** was solved by using direct methods.[8] For **3B**, the phosphorus position, determined by Patterson techniques, was used as a known fragment in the program DIRDIF.[9] Full-matrix least-squares refinement procedures were used for **3A** and for **3B**.[10] For **3A**, hydrogen atoms, with the exception of the amine hydrogen, H(1), were included in idealized positions riding on the atoms to which they are attached. For **3B**, hydrogen atoms were included in observed positions, riding as above.

## Results and Discussion

The diazaphosphole oxide **3** forms in high yield (>85%) from the reaction of 1,2-$(NH_2)_2C_6H_4$ with $PhP(O)PCl_2$,[5] in moderate yield (33%) from the reaction of 1,2-$(NH_2)_2C_6H_4$ with $PhP(OPh)_2$, and in minute quantity from the trace $H_2O$ hydrolysis of the cyclotetraphosphazane $[C_6H_4N_2(PhP)_2]_2$ or its reaction mixture. The $[C_6H_4N_2(PhP)_2]_2$ hydrolysis reaction is serendipitous, and we have not yet determined the conditions necessary to make it synthetically viable.

The 1,2-$(NH_2)_2C_6H_4/PhP(OPh)_2$ reaction is likely complex. The $^{31}P$ NMR spectral data indicate that the P(III) diazaphosphole **2** (R = Ph) might form as an intermediate since a transient singlet resonance at $\delta$ 110 (**4**) in the region characteristic of diazaphospholes is seen.[11] However, we have been unable to isolate this product. Although traces of $PhP(O)(OPh)_2$ are invariably present in the $PhP(OPh)_2$ (<5%), more **3** is formed than can be accounted for by the 1,2-$(NH_2)_2C_6H_4/PhP(O)(OPh)_2$ reaction. It is possible that **3** forms as

$$1,2\text{-}(NH_2)_2C_6H_4 + PhP(OPh)_2 \rightarrow PhOH + PhH + C_6H_4(NH)_2P(O)Ph \quad (1)$$

a process in which stepwise oxidative addition[12] of a $C_6H_4(NH_2)_2$ N–H bond to $PhP(OPh)_2$, elimination of phenol,[13] and finally elimination of benzene occurs. That **3** forms in the $PhP(OPh)_2/(NH_2)_2C_6H_4$ reaction is interesting, since the analogous $MeC_6H_4P(OPh)_2/(NH_2)_2C_6H_4$ reaction of Pilgram and Korte[3] was reported to give the P(III) product $C_6H_4(NH)_2PC_6H_4Me$. However, since their characterization was limited to elemental analytical data (found[3] wt % of C, H, N, and P 61.86, 5.86, 11.34, and 12.38, respectively), which upon recalculation better fit the oxide $C_6H_4(NH)_2P(O)C_6H_4Me$ (calculated wt % 63.93, 5.36, 11.50, and 12.69, respectively), we conclude that they might in fact have isolated the P(V) oxide instead of the P(III) product.

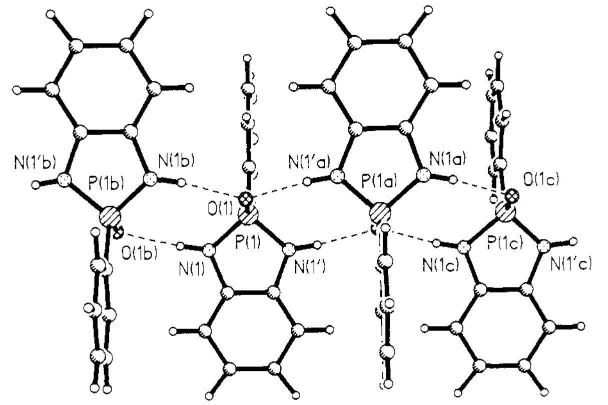

**Figure 2.** Segment of **3A** packing in the lattice, showing the intermolecular H-bonding. Symmetry positions are denoted as follows: (prime) $x, {}^1/_2 - y, z$; (a) $1 - x, -y, 2 - z$; (b) $1 - x, 1 - y, 2 - z$; (c) $x, y - 1, z$.

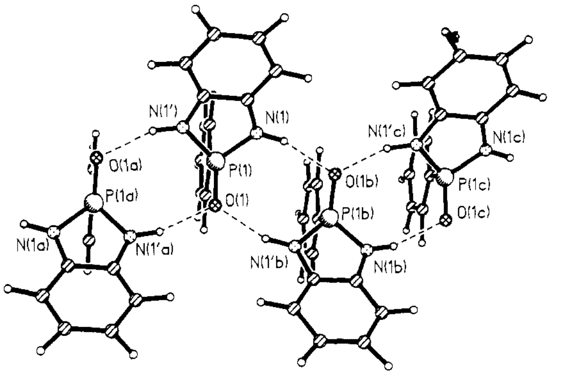

**Figure 3.** Segment of **3B** packing in the lattice, showing the intermolecular H-bonding. Symmetry positions are denoted as follows: (prime) $x, y, z$; (a) $-{}^1/_2 - x, y, {}^1/_2 - z$; (b) ${}^1/_2 + x, y, {}^1/_2 - z$; (c) $1 + x, y, z$.

**Table IV.** Selected Bond Distances (Å) and Angles (deg) for $C_6H_4(NH)_2P(O)Ph$ (**3A** and **3B**)

| | **3A** | **3B** |
|---|---|---|
| | (a) Distances | |
| P(1)–N(1) | 1.651 (2) | 1.655 (4) |
| P(1)–O(1) | 1.486 (2) | 1.485 (5) |
| P(1)–C(1) | 1.778 (3) | 1.784 (8) |
| N(1)–C(7) | 1.406 (2) | 1.396 (7) |
| C(1)–C(2) | 1.376 (4) | 1.381 (12) |
| C(6)–C(1) | 1.382 (4) | 1.392 (12) |
| C(7)–C(7)′ | 1.388 (5) | 1.395 (10) |
| C(7)–C(8) | 1.377 (3) | 1.382 (7) |
| C(8)–C(9) | 1.398 (3) | 1.380 (8) |
| C(9)–C(9) | 1.366 (6) | 1.373 (12) |
| | (b) Angles | |
| C(1)–P(1)–O(1) | 109.7 (1) | 109.8 (4) |
| O(1)–P(1)–N(1) | 116.9 (1) | 117.1 (2) |
| N(1)–P(1)–N(1) | 92.6 (1) | 92.0 (3) |
| C(1)–P(1)–N(1) | 109.8 (1) | 109.8 (3) |
| P(1)N(1)–C(7) | 112.2 (1) | 112.5 (3) |
| P(1)–C(1)–C(2) | 120.6 (2) | 118.8 (7) |
| C(6)–C(1)–C(2) | 119.2 (3) | 119.7 (8) |
| P(1)–C(1)–C(6) | 120.2 (2) | 121.5 (7) |
| N(1)–C(7)–C(7)′ | 10.8 (1) | 110.7 (4) |
| C(7)′–C(7)–C(8) | 121.2 (2) | 120.4 (5) |
| N(1)–C(7)–C(8) | 128.1 (2) | 128.9 (4) |
| C(7)–C(8)–C(9) | 117.8 (2) | 118.5 (5) |
| C(8)–C(9)–C(9)′ | 121.1 (2) | 121.0 (6) |

Compound **3**, from the $PhP(OPh)_2/(NH_2)_2C_6H_4$ reaction mixture or $CHCl_3$ solvent,[4,5] crystallizes as polymorph **3A**, whereas the compound obtained from the $[C_6H_4N_2(PhP)_2]_2$ reaction mixture is a second polymorph, **3B**. Both have been structurally characterized by single-crystal X-ray studies. **3A** and **3B** crystallize in orthorhombic *Pnma* and *Cmca* space groups with four

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and eight atoms per unit cell, respectively. The structure of **3A** and **3B** is shown in Figure 1. The packings of the two polymorphs in their lattices are shown in Figures 2 and 3. **3A** or **3B** contains a planar $C_6N_2$ unit; however, the PhP phosphorus is displaced slightly out of the plane. The $C_6N_2/N_2P$ interplane angle in **3A** and **3B** is 11°. In each case the plane of the phenyl group on phosphorus is perpendicular to the $C_6N_2$ plane. Bond distances and bond angles (Table IV) between **3A** and **3B** vary only slightly and are within the ranges of bond angles observed in other P(V) phosphorus-nitrogen compounds.[14,15] In both cases, each molecule is H-bonded from the P=O oxygen to the N—H bond units on each of two adjacent $C_6H_4(NH)_2P(O)Ph$ molecules in the lattice. Each oxygen is hydrogen-bonded to two N—H units, and each N—H unit is H-bonded to one P=O group.

**3A** and **3B** do not differ significantly in basic molecular parameters or lattice H-bonding but rather in the detail of how complete molecules are oriented relative to one another in the lattice. In **3B** the molecules are arranged such that the phenyl groups of each $C_6H_4(NH)_2P(O)C_6H_5$ are pointing in the same direction, creating a two-dimensional planar structure with planar, stacked phenyl groups. In contrast, **3A** has molecules alternatively rotated such that the phenyl groups alternate from one side to the other of each layer. Again the phenyl groups stack in a parallel fashion; however, they are between molecules in alternate layers. The parallel phenyl rings in **3A** and **3B** are separated by 3.80 and 3.82 Å, respectively. **3A** and **3B** are not common types of conformational polymorphs[16,17] but rather are a rarer form where lattice differences occur as a result of complete molecular rotations in the lattice.

Organic and organometallic solids that contain parallel-stacked planar $\pi$ electron-rich rings are of interest for their electrical,[18] electrooptic,[19,20] and magnetic properties.[20] In these, layered packing can occur in a fortuitous way or as a result of features contained by the molecules that aid in the development of layered stacking, e.g. metal atom of H-bonding links between packing units. Polymorphs **3A** and **3B** appear to be ordered by intermolecular H-bonding interactions. It is likely that a variety of planar aromatic groups can be attached to the phosphorus atom of the 1,3-dihydro-1,3,2-diazaphosphole unit to form new stacked arene ring systems. In addition, substitution of one ortho or meta H on the $C_6H_4$ phenylene ring would produce asymmetric diazaphospholes, which could pack in acentric space groups.[20] Studies to obtain such materials are in progress currently.

**Acknowledgment**. Support for this work by the National Science Foundation (Grant CHE-8312856), the Colorado Advanced Materials Institute, and a fellowship for E.G.B. from the Dow Chemical Foundation is gratefully acknowledged.

**Registry No.** 3, 7597-43-5; 1,2-$(NH_2)_2C_6H_4$, 95-54-5; $PhP(OPh)_2$, 13410-61-2.

**Supplementary Material Available:** Listings of all crystal data, collection parameters, and refinement details, hydrogen atom coordinates, thermal parameters, bond distances and angles, and least-squares planes and deviations from planes (9 pages); listings of structure factors (6 pages). Ordering information is given on any current masthead page.

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# A Stable $\mu$-Peroxo Complex of Rhodium(II) Intercalated in the Interlamellar Spaces of Montmorillonite. Solid-State $^{27}$Al, $^{29}$Si, and $^{31}$P NMR and EPR Investigation

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The first dioxygen complex of a formal Rh(III) coordinated to $O_2^{2-}$ was reported[1,2] by the oxidative addition of $O_2$ on the Rh(I) complex $RhCl(PPh_3)_3$. Several diamagnetic cationic complexes of Rh(III) with chelated phosphines and arsines and a 1:1 stoichiometry of Rh(III):$O_2^{2-}$ were later reported.[3-7] Though the paramagnetic dioxygen complexes of cobalt(III) are numerous and well established,[8,9] the corresponding paramagnetic complexes of Rh(III) are comparatively rarer[10-12] and can be formally considered as the complexes of Rh(III) with the superoxide ion $O_2^-$. The rhodium porphyrin complexes $(P)Rh(O_2)$ (P = tetraphenylporphyrinate, octaethylporphyrinate) are also paramagnetic[13-15] with a formal coordination of $O_2^-$ to Rh(III). Paramagnetic Rh(III) superoxo complexes were also obtained[16] by the oxygenation of Rh(II) complexes. There is, however, only one report[17] of a Rh(II) superoxo complex obtained as a paramagnetic species in the oxygenation of $[Rh(dppe)_2]BF_4$ (dppe = 1,2-bis(diphenylphosphino)ethane).

We describe in the present note the formation of the novel $\mu$-peroxo Rh(II) complex by the oxygenation of cationic $[Rh(PPh_3)_3]^+$ species trapped in the hydration layer of montmorillonite. The unusual geometry imparted to the rhodium centers by intercalation makes viable the formation of the $\mu$-peroxo Rh(II) species. The complex has been characterized by IR, EPR, ESCA, X-ray, and solid-state $^{27}$Al, $^{29}$Si, and $^{31}$P NMR spectroscopy. Oxygenation of Wilkinson's complex outside the lattice gives the well-defined $RhCl(O_2)(PPh_3)_3$ and the dimeric $[RhCl(PPh_3)_2O_2]_2$ complexes.

## Experimental Section

Rhodium trichloride was purchased from Johnson Matthey, and triphenylphosphine and montmorillonite clay were obtained from Fluka A. G. A nominal chemical composition of montmorillonite used in present investigation (weight percent) is as follows: $SiO_2$, 70%; $Al_2O_3$, 15%; $Fe_2O_3$, 1.5%; CaO, 2.5%; MgO, 3.0%; $Na_2O$, 0.5%; $K_2O$, 1.5% (loss on ignition 6%). All organic solvents used were obtained from BDH and were purified by known methods prior to use. Argon gas was used for maintenance of an inert atmosphere and was used without purification. IR and far-IR spectra were recorded as KBr disks and as Nujol mulls dispersed in polyethylene films, respectively, on a Nicolet 200 SXV

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