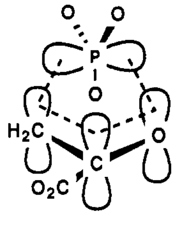
stereochemical course of the sigmatropic rearrangement involving concerted C to O 1,3-phosphoryl migration should be governed by orbital topology control.[11] As such, this four-electron, ground state pericyclic process would favor transition state **3** with a



3

Mobius topological orbital array corresponding to inversion at phosphorus.[12] Consequently, the observed stereochemical outcome strongly suggests that PEP-phosphomutase not only catalyzes a unique C–P bond-forming biosynthetic process but also employs a remarkably interesting pericyclic reaction mechanism.

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Synthesis and X-ray Structures of Compounds Having Very Short Phosphorus-Phosphorus Single Bonds: How Much of the Shortening in P-P Double Bonds Is Due to p-p π-Overlap?

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The classical model for double bonding in main group compounds involves a σ- and a π-bond.[1] Moreover, the difference in length between double and single bonds is often said to be due to the π-overlap. This simplistic picture has been modified to take account of the change in hybridization in the σ-bonding orbitals. For carbon–carbon bonds it is thought that about 70–75% of the shortening is due to p–p π-overlap, whereas 25–30% can be accounted for by the change in hybridization in the σ-orbitals from sp^3 to sp^2.[2] Consider now the case of the recently synthesized diphosphenes RP=PR[3,4] that have the P–P double bond distances of about 2.02 Å in comparison to P–P single bond lengths of ca. 2.22 Å. This contraction is also thought to be due mainly to a π-bond formed by side-on overlap of p-orbitals on the P atoms. However, the difference in hybridization between a diphosphane such as R_2PPR_2 and a diphosphene RPPR is even greater than that in carbon as the angles found in trivalent phosphorus compounds are considerably lower than tetrahedral values. The question that then arises is as follows: how much of the shortening in diphosphenes is due to the conventional p–p π-overlap and how much is due to the change in hybridization? In this paper an attempt is made to answer this question by the synthesis, spectroscopic, and structural characterization of the first examples of 1,1′-diboryldiphosphanes, the dimers $[PRBMes_2]_2$ (R = 1-Ad, **1**; R = Mes, **2**)[5] that may illustrate the relative contributions of rehybridization and p–p π-overlap to P–P double bond strength.

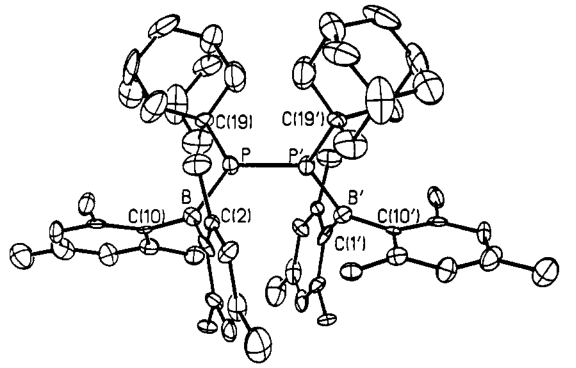

Figure 1. Computer-generated drawing of **1**, H atoms omitted for clarity. Selected bond distances (Å) and angles (deg) are as follows: P–P′ = 2.109 (4), B–P = 1.852 (9), B–C(1) = 1.570 (12), B–C(10) = 1.599 (12), P–C(19) = 1.893 (8), C(1)–B–P = 119.3 (6), C(10)–B–P = 118.3 (6), C(1)–B–C(10) = 122.3 (7), B–P–C(19) = 120.5(4), B–P–P′ = 118.3 (3), C(19)–P–P′ = 120.6 (3).

The compounds **1** and **2** were synthesized,[6] in moderate yield, by the oxidation of the phosphinideneborate precursors $Li(Et_2O)_2PRBMes_2$ (R = 1-Ad or Mes) using $CrCl_3$. Both compounds were characterized by ^1H, ^{11}B, and ^{31}P NMR spectroscopy, and the X-ray crystal structure of **1**[7] is illustrated in Figure 1. Important structural parameters are given in the figure caption. There is a 2-fold rotation axis through the P–P′ bond, which has a length of 2.109 (4) Å. (The incompletely refined structure of **2** also indicates a P–P distance of 2.11 Å.)[7] Both the boron and phosphorus centers are essentially planar (dihedral angle = 25.5°). There is also a large dihedral angle of 70.5° between the P and

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(1) This view of double-bonding does not hold in the case of the heavier main group 4 analogues: Hitchcock, P. B.; Lappert, M. F.; Miles, S. J.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1984**, 480. Goldberg, D. E.; Hitchcock, P. B.; Lappert, M. F.; Thomas, K. M.; Fjelberg, T.; Haaland, A.; Schilling, B. E. R. *J. Chem. Soc., Dalton Trans.* **1986**, 2387. For calculations on disilenes, see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *12*, 1201. Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419 and references therein.

(2) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 19. The bond lengths given in this reference are as follows: C–C single bonds; sp^3–sp^3 = 1.54 Å; sp^2–sp^2 = 1.48 Å, and C–C double bond in ethylene = 1.34 Å. Thus, the double bond is 13% shorter than a sp^3–sp^3 single bond, but the rehybridization is said to account for a 3.9% shortening (1.54–1.48 = 0.06 Å) or 30% of the overall contraction.

(3) Yoshifuji, M.; Shima, I.; Inamoto, N.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 4587.

(4) Cowley, A. H. *Polyhedron* **1984**, *3*, 389; *Acc. Chem. Res.* **1984**, *17*, 386. Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1.

(5) 1-Ad = 1-adamantyl, Mes = 2,4,6-$Me_3C_6H_2$–.

(6) The synthesis of **1** is described here; compound **2** was synthesized similarly. Under anaerobic and anhydrous conditions $Mes_2BP(Ad)Li(Et_2O)_2$ (1.02 g, 1.79 mmol) in THF (35 mL) was added dropwise at 0 °C to a suspension of $CrCl_3$ (0.26 g, 1.80 mmol) in THF (30 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. All volatiles were removed under reduced pressure, and the brown-greenish residue was taken up in pentane (~150 mL). Filtration through Celite gave an intense yellow solution and a green-gray solid residue on the filter. Partial reduction of volume to ~85 mL, followed by slow cooling in a –20 °C freezer produced dark yellow crystals of **1**, suitable for X-ray structure determination. Further volume reduction, ~15 mL, gave a total yield of 0.41 g (48%) of **1**: mp 323–325 °C (dec); ^1H NMR (300 MHz, $CDCl_3$) $\delta = 6.73$ and 6.64 (2 s, 2 H each = meta-H), 2.34, 1.98, 1.87 (br s, adamantyl) 2.23, 2.17, 1.55, 1.51 (s, ortho and para H); ^{11}B NMR (96.25 mHz, C_6D_6) $\delta = 49.3$ ($J_{B-P} = 50$ Hz); ^{31}P NMR (145.73 MHz, hexane C_6H_{14}) $\delta = 2.8$. **2**: 247–250 °C (dec); ^1H NMR (300 MHz, C_6D_6) $\delta = 6.6$ (br s = meta-H), 3.2 q and 1.05 t (due to ethers of crystallization), 2.25, 2.07, 1.85 (br s ortho and para-H); ^{11}B NMR (96.25 MHz, C_6D_6) $\delta = 54.0$; ^{31}P NMR (145.73 MHz, C_6D_6) $\delta = -22.3$.

(7) Crystal data for **1**, at 130 K with Mo Kα ($\lambda = 0.71069$ Å) radiation; $a = 20.953$ (7) Å; $b = 33.824$ (6) Å; $c = 13.596$ (5) Å, orthorhombic, space group *Fdd*2; $Z = 8$ (dimers); 1113 unique observed ($I > 3\sigma(I)$) data $R = 0.058$. Crystal data for **2** could not be refined to an R value less than 0.19. This is primarily due to the inclusion of disordered Et_2O and, perhaps, pentane molecules in the crystal lattice. A reasonable model for the disorder was not found. The current state of refinement affords a P–P bond length of 2.11 Å with planar phosphorus centers which is in good agreement with the data for **1**. Crystal data for **2** at 130 K with Mo Kα ($\lambda = 0.71069$ Å) radiation: $a = 19.801$ (8) Å, $b = 23.210$ (8) Å, $c = 24.198$ (8) Å orthorhombic space group *Pbca*; $Z = 8$ (dimers); 2899 unique observed ($I > 2\sigma(I)$) data.

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P′ planes. The boron–phosphorus distance is 1.852 (9) Å, close to that seen in similar monomeric organophosphinoboranes.[8] The angles at the B and P centers do not deviate more than 1.7° from the regular trigonal values. The boron–carbon distances are similar to those in other boron mesityl species.[9] The phosphorus–carbon bond is not particularly short although there appears to be few trivalent phosphorus adamantyl derivatives available for comparison.

The major structural features of interest in **1** concern (a) the short P–P′ bond length, (b) the planarity of the phosphorus centers, and (c) the large twist angle between the phosphorus planes. Point (c) tends to discredit the analogy between **1** and butadiene which might have accounted for some of the observed shortening in the P–P′ bond in terms of orbital interactions between the π-orbital systems of the B–P bonds. It is notable that the B–P bond still has considerable multiple character[10] as indicated by the B–P distance of 1.852 (9) Å, although the dihedral angle between the B and P planes is somewhat larger (presumably for steric reasons) than those previously observed. The planar nature of the phosphorus and the short B–P bond indicates that there is significant lone pair interaction with the empty p-orbital on boron.

Regarding point (b), the nearly regular trigonal-planar angles at phosphorus indicate that hybridization is close to sp^2. Thus, **1** differs from normal diphosphanes which often display angles at phosphorus that are much less than tetrahedral, indicating reduced s-character (significantly less than sp^3) in the bonding orbitals. These differences in bond angles point to sp^2–sp^2 orbital overlap for the P–P′ bond in **1** instead of overlap between orbitals with substantially more p (and less s) character as in "normal" diphosphanes. Such differences in hybridization are thought to cause significant variation in C–C bond lengths in hydrocarbons.[2] It seems reasonable to assume that the greater hybridization differences in phosphorus compounds could give rise to larger variation in P–P bonds.

In connection with point (a) it could be argued that the short P–P′ bond arises from a reduction in phosphorus lone pair–lone pair repulsion as a result of the interaction with the empty boron p-orbital. Interelectronic repulsion is probably reduced, but calculations and experimental data on *cis*- and *trans*-diphosphenes give almost identical P–P distances which suggest that the repulsions play a minor role. The phosphorus–phosphorus bond length in **1**, 2.109 (4) Å, which is the shortest P–P single bond reported to date,[11] is marginally closer to the average length of a P–P double bond than to that of a single bond. For example, the first P–P double bond to be structurally characterized[3] had a length of 2.034 (2) Å, whereas P–P single bonds are about 2.22 Å long.[12] Nonetheless, the P–P bond in **1**, owing to the structural configuration of the molecule, must be regarded as a single bond as it involves only one orbital from each phosphorus. Further evidence for this assignment comes from the ^{31}P NMR spectra of **1** and **2** that show singlets at 2.8 and −22.3 ppm. These values are far from those seen in the doubly bonded compounds which generally appear several hundred ppm downfield.[4] Instead, they are much closer to the shifts for normal diphosphanes which often appear at δ values between 0 and −100 ppm.[13]

In summary, it appears that the answer to the title question is that the shortening in diphosphenes is about equally divided between p–p π-overlap and rehybridization of the σ-orbitals. Calculations on the hypothetical species *trans*-HPPH seem to bear out these experimental data.[4] The most recent[14] showed that the bonding π-orbital in this species (which is the HOMO) appears at an energy of 9.69 eV below the LUMO, whereas the stabilization of the σ(PP) bond is 25.02 eV. In addition, estimates of the rotational barrier in diphosphenes vary from 20 to 35 kcal mol^{-1},[4,14,15] whereas the strength of the π-bonds in alkenes is in the 50–60 kcal mol^{-1} [16] range which is in good agreement with the respective proportions of contraction due to p–p π-overlap. Other support comes from calculations[17] on the hypothetical diphosphene transition-metal complex, $H_2P_2Cr(CO)_5$, that indicate a large amount (0.3 electrons) of back-donation by the metal fragment into the b$_g$ (π^*-type) orbital of the ligand. However, this extensive transfer of electron density into the ligand antibonding orbital results in only slight lenghtening of the P–P bond upon complexation. This result, which is in agreement with structural and spectroscopic studies, is consistent with weaker p–p orbital interactions.[4,18]

Acknowledgment. We thank the National Science Foundation (CHE-8618739) for financial support.

Supplementary Material Available: Tables of crystallographic data, summary of data collection and refinement, bond distances and angles, anisotropic thermal parameters and hydrogen coordinates (8 pages); table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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[8] Feng, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1986**, *25*, 4615. B–P distance = 1.859 (3) Å.

[9] The structures of numerous compounds involving the $-BMes_2$ and related groups bonded to phosphorus have appeared in the literature. See ref 8 and Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817. Olmstead, M. M.; Power, P. P.; Weese, K. J.; Doedens, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 2541. Bartlett, R. A.; Feng, X.; Olmstead, M. M.; Power, P. P.; Weese, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4851.

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[11] Niecke, E.; Rüger; Krebs, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 544. Binger, P.; Biedenbach, B.; Krüger, C.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 764. Barron, A. R.; Cowley, A. H.; Hall, S. W.; Nunn, C. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 837. These publications also feature short P–P distances of 2.129 Å, 2.147 (1) Å and 2.118 (3) Å as part of the highly strained cage compounds. Calculations have accounted for this phenomenon in terms of olefinic character. See: Schoeller, W. W.; Staemmler, V.; Rademacher, P.; Niecke, E. *Inorg. Chem.* **1984**, *25*, 4382.

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[13] Mark, V.; Dungan, C. H.; Crutchfield, M. M.; van Wazer, J. R. *Topics in Phosphorus Chemistry*; Grayson, M., Griffith, E. J., Eds.; Wiley: New York, 1967; Vol. 5, Chapter 4.

[14] Allen, T. L.; Scheiner, A. C.; Yamaguchi, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1986**, *108*, 7579. These and earlier calculations also indicate that lone-pair/lone-pair repulsions probably play only a minor role in the determination of the P–P bond length. For example, there are only small differences in the P–P distance of the cis and trans isomers of HPPH.

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[17] Schugart, K. A.; Fenske, R. F. *J. Am. Chem. Soc.* **1985**, *107*, 3384.

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Exclusive Abstraction of Nonexchangeable Hydrogens from DNA by Calicheamicin $\gamma 1^{I}$

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The calicheamicins[1] are potent antitumor antibiotics that are believed to mediate their DNA damaging properties and cytotoxicity primarily via oxidative strand scission.[2] In vitro calicheamicin $\gamma 1^{I}$ (**1**), in the presence of thiols, produces double strand cuts in supercoiled, covalently closed circular DNA, in DNA restriction fragments, and in synthetic oligomers with a high degree of sequence specificity.[2,3] It has been proposed that DNA scission

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