(2 H, m), 2.5 (4 H, m), 1.0 (4 H, m). HRMS calcd for $C_{20}H_{24}MoO_6$: $M^+ = 456.0621$. Found: $M^+ = 456.0620$.

39d (mp 148–150 °C (dec)). IR (CCl_4): ν_{max} 1953, 1877, 1743 cm^{-1}. NMR ($CDCl_3$): δ 5.27 (5 H, s), 4.17 (1 H, t, $J = 7$ Hz), 3.68 (6 H, s), 3.57 (2 H, m), 2.51 (4 H, d, $J = 7.6$ Hz), 2.32 (2 H, t, br, $J = 6.8$ Hz), 0.92 (1 H, dt, $J = 14.4$, 6.7 Hz), 0.72 (1 H, d, br, $J = 14.4$ Hz). Anal. Calcd for $C_{19}H_{22}MoO_6$: C, 51.59; H, 5.01. Found: C, 51.63; H, 5.16.

Determination of X-ray Structure for Complex 33. A yellow elongated plate of $C_{29}H_{39}MoSiNO_5S$ having approximate dimensions of 0.24 × 0.20 × 0.04 mm was mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius diffractometer. The monoclinic cell parameters and calculated volume are as follows: $a = 16.398$ (4), $b = 8.369$ (1), $c = 22.239$ (5) Å; $\beta = 90.78$ (2)°; $V = 3051.8$ Å^3. For $Z = 4$ and FW = 637.73, the calculated density is 1.39 g/cm^3. The space group was determined to be $P2_1/n$ from systematic absences.

A total of 6651 reflections were measured of which 6421 were unique and not systematically absent. The data were corrected for decay (2.6%), absorption ($\mu = 5.6$ cm^{-1}), and Lorentz and polarization. The structure was solved using Patterson and Fourier techniques. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least squares to a final $R = 0.043$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w, is defined as $4F_o^2/\sigma^2(F_o)^2$. Scattering factors were taken from Cromer and Waber,[20] and anomalous dispersion coefficients, from Cromer.[21] All calculations were carried out on a VAX 11/750 computer with SDP/VAX.[22]

Details of data collection and structure solution are given in Table IV, final atomic parameters in Table V, and derived bond lengths and angles in Tables VI and VII. A perspective view of complex **33** is presented in Figure 1.

A complete report of the structure determination, tables of anisotropic temperature factors, and lists of observed and calculated structure factors are available as supplementary material.

Acknowledgment. A.J.P. thanks the U.S. Public Health Service and the National Institutes of Health for financial support of this research (Grants GM 34159 and GM 32114). High-field NMR and mass spectrometer facilities were obtained through grants from the National Science Foundation (CHE 80-24633) and National Institutes of Health (RR-01689 and RR-03574). A.A.P. thanks the College of Arts and Sciences, University of Toledo, for support of the X-ray crystallographic facility.

Supplementary Material Available: Structural report for the X-ray structure determination of complex **33**, giving a description of experimental procedures, data collection, data reduction, and structure solution and refinement, tables of general temperature factor expressions and torsional angles, and a drawing of complex **33** (7 pages); listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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(20) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(21) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(22) Frenz, B. A. "*The Enraf-Nonius CAD 4 SDP—A Real-time System for Concurrent X-ray Data Collection and Crystal Structure Determination*" In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University: Delft, Holland, 1978; pp 64–71.

Boron–Phosphorus Analogues of Benzene and Cyclobutadiene. Synthesis and Characterization of the Boraphosphabenzenes $(RBPR')_3$ (R = Mes, Ph; R′ = Ph, Mes, C_6H_{11}, *t*-Bu) and the Diphosphadiboretane $(ThexylBPMes)_2$

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Abstract: The synthesis and characterization of a range of boraphosphabenzenes having the formulas $(MesBPPh)_3$ (**1**), $(MesBPC_6H_{11})_3$ (**2**), $(MesBPMes)_3$ (**3**), $(MesBP\text{-}t\text{-}Bu)_3$ (**4**), and $(PhBPMes)_3$ (**5**) and a diphosphadiboretane of formula $(ThexylBPMes)_2 \cdot {}^2/_3Et_2O$ (**6**) are described (Mes = 2,4,6-$Me_3C_6H_2$, Thexyl = $(CH_3)_2CH((CH_3)_2C)$. The complete X-ray crystal structures of **1** and **6** are also reported and discussed in conjunction with the structure of **2**, which has appeared in a preliminary report. The main features of the structures of **1** and **2** are (i) the $B_3P_3C_6$ cores are planar, (ii) the B–P bonds are all equal, and (iii) the B–P bonds are short, averaging 1.84 Å. The four-membered-ring compound **6** has a planar B_2P_2 core with planar boron but pyramidal phosphorus centers. All the BP bonds are equal but they are significantly longer (ca. 1.9 Å) than those seen in **1** and **2**. Compounds **1–5** are the first examples of boraphosphabenzenes, the boron–phosphorus analogues of borazine and benzene. Compound **6** is the first structurally characterized diphosphadiboretane with no π-donor substituents (other than phosphorus) on boron. Both the X-ray structural and ^{11}B, ^{31}P, and ^1H NMR data for **1–5** support highly delocalized bonding and indicate considerable aromatic character. On the other hand, the nonplanar nature of the phosphorus centers in the cyclobutadiene-like **6**, the lengthened B–P bonds, and the very different ^{11}B and ^{31}P NMR observed chemical shifts support a bonding picture with considerably less delocalization. In effect, the π-bonding in **6** may be considered antiaromatic. This further supports the aromatic characteristics suggested for compounds **1–5**. Crystal data for **1** and **6** with Mo Kα radiation ($\lambda = 0.71069$ Å) at 130 K: (**1**) $a = b = 22.738$ (8) Å, $c = 13.729$ (3) Å, trigonal, space group $R\bar{3}$, $Z = 6$, $R = 0.047$; (**6**) $a = b = 31.046$ (11) Å, $c = 9.829$ (2) Å, trigonal, space group $R\bar{3}$, $Z = 9$, $R = 0.108$. A table of ^{11}B and ^{31}P NMR data for compounds **1–6** is provided and discussed in the context of the most closely related known boron–phosphorus compounds. In addition, incomplete X-ray crystal structures of compounds **3–5** together with explanatory notes are provided in the Supplementary Material. Crystal data for **3**, **4**, and **5** with Mo Kα radiation at 130 K: (**3**) $a = 18.020$ (4) Å, $b = 12.161$ (3) Å, $c = 28.245$ (8) Å, $\beta = 93.53$ (2)°, monoclinic, space group $P2_1/c$; (**4**) 26.072 (7) Å, $\beta = 21.645$ (5) Å, $c = 16.991$ (5) Å, $\beta = 113.90$ (2)°, monoclinic, space group $C2/c$; (**5**) $a = b = 22.810$ (5) Å, $c = 13.694$ (8) Å, trigonal, space group $P\bar{3}$.

Borazine, $(HBNH)_3$, the boron–nitrogen analogue of benzene, was first reported in 1926 by Stock and Pohland.[2] In the intervening years both borazine and related molecules have attracted considerable interest, mainly due to their isoelectronic relationship

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to benzene and its derivatives.[3] Borazine and benzene do indeed have many similar physical properties.[4] However, these resemblances do not extend to their chemistry. This is thought to be due to the more polar nature of the B–N bond, which disrupts the aromatic character. More recently, other cyclic BN compounds, for example, the diazadiboretidines $(RBNR')_2$ (R/R′ = *i*-Pr/*t*-Bu, *t*-Bu/*t*-Bu)[5] and even monomeric compounds such as *t*-BuB≡N-*t*-Bu[6] have appeared in the literature.

In contrast, the information concerning their boron–phosphorus analogues has remained sparse. There are no structurally characterized boron–phosphorus analogues of the monomer RB≡NR′ such as RB≡PR′. The current evidence for the existence of this species has come from mass spectrometry in the gas phase.[7] On the other hand, a few examples of the dimeric diphosphadiboretanes $(RBPR')_2$ are known in the form of their amido-substituted derivatives $(R_2NBPR')_2$, and the structures $[tmpBPMes]_2$,[8] $[tmpBPAr]_2$[7] (Ar = 2,4,6-*t*-$Bu_3C_6H_2$), and $[tmpBPCEt_3]_2$[9] (tmp = 2,2,6,6-tetramethylpiperidine) have been reported. However, no simple derivatives of the type $(RBPR')_2$, where R or R′ was a non-π-donor substituent, have been well characterized. Similarly, until a preliminary report from this laboratory, boron-phosphorus analogues of borazine were unknown.[10] The scarcity of data on such boron–phosphorus compounds has thus provided a major impetus for the synthesis and characterization of the title compounds.

The first boraphosphabenzene, $(MesBPC_6H_{11})_3$ (**2**), was obtained during the attempted synthesis of $MesB(PHC_6H_{11})_2$ by the reaction of $MesBBr_2$ with 2 equiv of $C_6H_{11}PHLi$. This was characterized by X-ray crystallography in addition to ^{11}B and ^{31}P NMR. Some details have appeared in a preliminary report.[10] This reaction type has now been studied in more detail, and some of the results we obtained are reported in this paper. The syntheses of $(MesBPPh)_3$ (**1**), $(MesBPC_6H_{11})_3$ (**2**), $(MesBPMes)_3$ (**3**), $(MesBP\text{-}t\text{-}Bu)_3$ (**4**), and $(PhBPMes)_3$ (**5**) as well as the four-membered-ring compound $(ThexylBPMes)_2 \cdot {}^2/_3Et_2O$ (**6**) are described along with their ^{31}P and ^{11}B NMR spectroscopic data. The crystal structures of **1**, **2**, and **6** are also discussed in detail along with the incomplete results of X-ray crystallographic analysis of the compounds **3**, **4**, and **5**.

Experimental Section

General Procedures. All experiments were performed by using either modified Schlenk techniques under N_2 or a Vacuum Atmospheres HE 43-2 drybox under argon. Solvents were freshly distilled under N_2 from Na/K alloy–benzophenone ketyl and degassed twice immediately before use.

The reagents $MesBBr_2$,[11] $ThexylBCl_2$,[12] $MesPH_2$,[13] and *t*-$BuPCl_2$[14] were prepared according to the literature methods. $PhBCl_2$ (Alfa), $C_6H_{11}PH_2$ (Alfa), $PhPCl_2$ (Alfa), and *n*-BuLi (Aldrich) were obtained commercially and used as received. $PhPH_2$ and *t*-$BuPH_2$ were prepared from their respective chlorides by $LiAlH_4$ reduction.

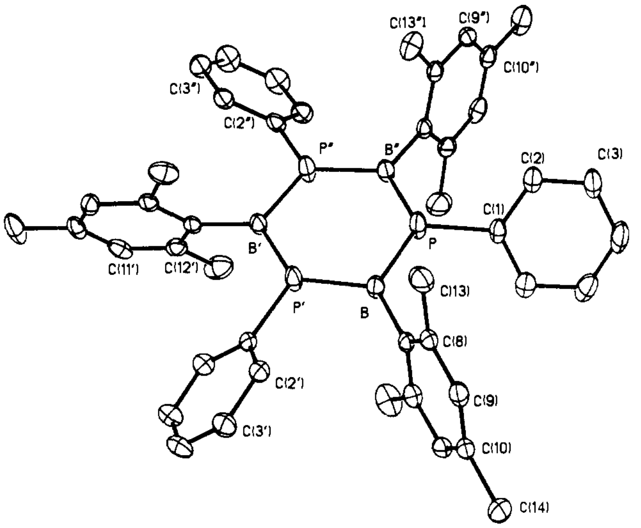

Figure 1. Computer-generated thermal ellipsoid plot of **1** (at 30% probability level). Important bond distances (Å) and angles (deg) are P–B = 1.839 (3), P–B″ = 1.845 (2), B–P′ = 1.844 (4), P–C(1) = 1.802 (3), B–C(7) = 1.567 (3), B–P–B″ = 124.5 (2), B–P–C(1) = 118.3 (1), C(1)–P–B″ = 115.5 (1), P–B–P′ = 114.9 (1), C(7)–B–P′ = 122.0 (2), and P–B–C(7) = 123.1 (2).

^{31}P and ^{11}B NMR spectra were obtained on a Nicolet NT-200 spectrometer operating at 81 and 64 MHz, respectively. All ^{31}P spectra were referenced to external 85% H_3PO_4 and recorded with 2-W proton decoupling unless otherwise noted. ^{11}B spectra were referenced to external $BF_3 \cdot OEt_2$. THF/C_6D_6 mixture was used as the solvent. ^1H NMR spectra were recorded on a QE-300 spectrometer operating at 300 MHz. All compounds gave satisfactory carbon and hydrogen analyses.

Synthesis of Compounds 1–6. $(MesBPPh)_3$ (1). $MesBBr_2$ (2.3 g, 7.9 mmol) in hexane (20 mL) was added dropwise at 0 °C to PhPHLi [prepared from $PhPH_2$ (1.74 g, 15.9 mmol) and 10 mL of 1.6 M *n*-BuLi in hexane] in Et_2O (40 mL). The resulting mixture was allowed to warm slowly to room temperature and stirred overnight. The volatiles were removed under reduced pressure, and the residue was extracted into a 1:1 hexane/toluene mixture. This was filtered, concentrated under reduced pressure, and cooled at 0 °C to obtain pale yellow crystals of **1**: yield 35%; mp >275 °C.

$(MesBPC_6H_{11})_3$ (2). The synthesis of this compound has been described in a preliminary communication,[10] and it was obtained in 48% yield: mp 324–325 °C.

$(MesBPMes)_3$ (3). $MesPH_2$ (1.4 g, 9.2 mmol) in Et_2O (30 mL) was metalated with *n*-BuLi (1.6 M, 5.8 mL) at 0 °C. This was stirred for 45 min, and $MesBBr_2$ (1.33 g, 4.6 mmol) in hexane (15 mL) was added dropwise. The color changed immediately to dark orange. The mixture was then stirred for 12 h at ambient temperature. Removal of volatiles under reduced pressure and extraction into hexane followed by filtration afforded a bright fluorescent orange/red solution. The solution was concentrated and cooled to −20 °C to obtain orange crystals of **3**: yield 29%; mp 334–337 °C. The bright color fades around 160 °C.

$(MesBP\text{-}t\text{-}Bu)_3$ (4). $MesBBr_2$ (2.1 g, 7.2 mmol) in hexane was added dropwise at 0 °C to *t*-BuPHLi (prepared from 1.3 g (14.4 mmol) of *t*-$BuPH_2$ and 9.1 mL of 1.6 M *n*-BuLi) in Et_2O (30 mL). An orange colored solution was obtained. The mixture was stirred overnight at room temperature, volatiles were removed under reduced pressure, and the residue was extracted into hexane. Filtration and reduction in volume of the filtrate followed by cooling at −20 °C gave orange-yellow dichroic crystals of **4**: yield 43%; softens at 275 °C and melts completely at 310 °C. A quantity of darker orange crystals was also obtained. Preliminary spectroscopic and structural data indicate that they are the four-membered ring species $(MesBP\text{-}t\text{-}Bu)_2$.

$(PhBPMes)_3$ (5). This was prepared from MesPHLi [from 1.34 g (8.8 mmol) of $MesPH_2$] and $PhBCl_2$ (0.7 g, 4.4 mmol) by a procedure very similar to that used for **1**. The yellow crystals of **5** were obtained

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(1) Fellow of the A. P. Sloan Foundation, 1985–1987.

(2) Stock, A.; Pohland, E. *Chem. Ber.* **1926**, *59*, 2215.

(3) Haiduc, I.; Sowerby, D. B. *The Chemistry of Inorganic Homo- and Heterocycles*, Academic: New York, 1987; Vol. 1, p 19. Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds; Springer-Verlag: Berlin, 1978; Vol. 14, p 48.

(4) Niedenzu, K.; Dawson, J. W. *Boron–Nitrogen Compounds*; Springer-Verlag: Berlin, 1965. Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: New York, 1986; p 238.

(5) Paetzold, P.; Plotho, Ch. v.; Schmid, G.; Boese, R. *Z. Naturforsch. B* **1984**, *39B* 1069. Schreyer, P.; Paetzold, P.; Boese, R. *Chem. Ber.* **1988**, *121*, 195. See also ref 6.

(6) Paetzold, P.; Plotho, Ch. v.; Schmid, G.; Boese, R.; Schrader, B.; Bougeard, D.; Pfeiffer, U.; Gleiter, R.; Schäfer, W. *Chem. Ber.* **1984**, *117*, 1089. See also: Paetzold, P. *Adv. Inorg. Chem.* **1987**, *31*, 123.

(7) Arif, A. M.; Boggs, J. E.; Cowley, A. H.; Lee, J.-G.; Pakulski, M.; Power, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 6083.

(8) Arif, A. M.; Cowley, A. H.; Pakulski, M.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1986**, 889.

(9) Kölle, P.; Nöth, H.; Paine, R. T. *Chem. Ber.* **1986**, *119*, 2681.

(10) Dias, H. V. R.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1270. However, some simple BP ring systems, for example $(PhBPPh)_2$, had already been reported, if not well characterized. See: Coates, G. E.; Livingstone, J. G. *J. Chem. Soc.* **1961**, 5053. In addition, a mixture of compounds of formula, $(PhBPPh)_n$, n = 3 or 4 had been reported: English, W. D. *Chem. Abstr.* **1962**, *57*, 11239. The major evidence for the degree of aggregation involved cryoscopic data. Also, molecular orbital calculations had shown that B–P analogues of borazine might be capable of existence: Brown, D. A.; McCormack, C. G. *J. Chem. Soc.* **1964**, 5385.

(11) Exner, O.; Folli, U.; Marcaccioli, S.; Vivarelli, P. *J. Chem. Soc., Perkin Trans. 2* **1983**, 757.

(12) Brown, H. C.; Sikorski, J. A. *Organometallics* **1982**, *1*, 28.

(13) Oshikawa, T.; Yamashita, M. *Chem. Ind.* (*London*) **1985**, 126.

(14) Wold, A.; Ruff, J. K. *Inorg. Synth.* **1973**, *14*, 4.

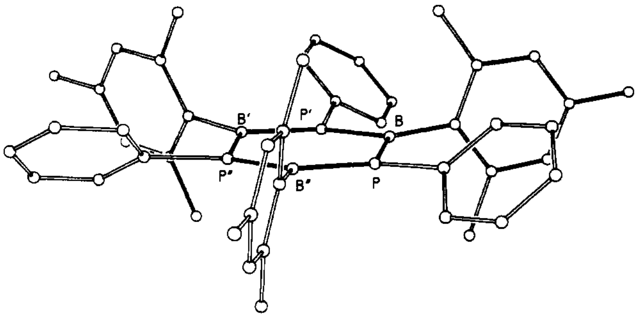

Figure 2. View of **1** showing planar $P_3B_3C_6$ core. (All the atoms were given arbitrary fixed-radius circles for clarity.)

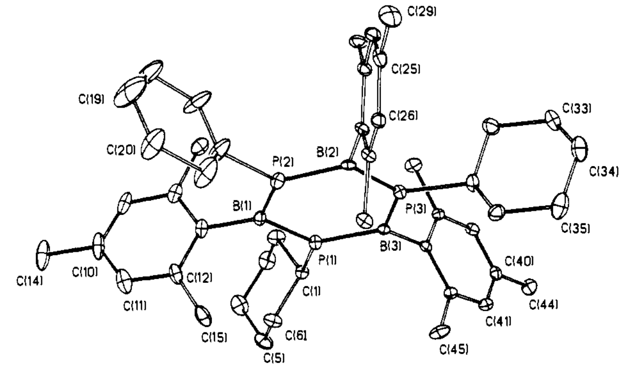

Figure 3. Computer-generated thermal ellipsoid plot of **2** (at 30% probability level). Selected bond distances (Å) and angles (deg) are B(1)–P(1) = 1.838 (6), P(1)–B(3) = 1.833 (6), B(3)–P(3) = 1.835 (6), P(3)–B(2) = 1.851 (6), B(2)–P(2) = 1.837 (7), P(2)–B(1) = 1.844 (7), B(1)–C(7) = 1.577 (8), B(2)–C(22) = 1.570 (8), B(3)–C(37) = 1.577 (8), P(1)–C(1) = 1.837 (6), P(2)–C(16) = 1.842 (7), P(3)–C(31) = 1.836 (6), P(1)–B(1)–P(2) = 114.8 (3), P(2)–B(2)–P(3) = 113.8 (3), P(1)–B(3)–P(3) = 116.0 (3), B(1)–P(1)–B(3) = 124.2 (3), B(1)–P(2)–B(2) = 126.0 (3), and B(2)–P(3)–B(3) = 125.0 (3).

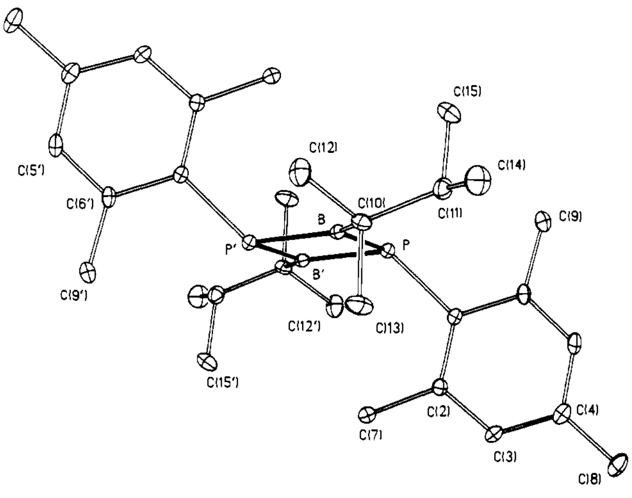

Figure 4. Computer-generated thermal ellipsoid plot of **6** (at 30% probability level). Important bond distances (Å) and angles (deg) are P–B = 1.898 (5), P–B′ = 1.896 (7), B–P′ = 1.896 (7), P–C(1) = 1.835 (4), B–C(10) = 1.577 (9), B–P–B′ = 87.7 (3), B–P–C(1) = 120.7 (2), C(1)–P–B′ = 122.9 (2), P–B–P′ = 92.3 (3), P–B–C(10) = 133.9 (4), and C(10)–B–P′ = 133.1 (4).

in 37% yield; slowly decomposes >250 °C.

(ThexylBPMes)$_2$·$^2/_3$Et$_2$O (6). ThexylBCl$_2$ (0.83 g, 5 mmol) in hexane (5 mL) was added dropwise to MesPHLi [from 1.52 g (10 mmol) of MesPH$_2$ and 6.2 mL of 1.6 M *n*-BuLi] in Et$_2$O (20 mL) at 0 °C. The solution was stirred overnight at room temperature. Then the volatiles were removed under vacuum, and the residue was extracted into hexane and filtered. The filtrate was concentrated under reduced pressure, Et$_2$O (2 mL) was added, and the mixture was cooled at −78 °C to obtain orange crystals of **6**: yield 39%; mp 98–100 °C.

X-ray Data Collection and the Solution and Refinement of the Structures. All X-ray data were collected with a Syntex P2$_1$ diffractometer equipped with a graphite monochromator and a modified LT-1 low-temperature device. Crystallographic programs used were those of SHELXTL, Version 5, installed on a Data General Eclipse computer. Scattering factors were from Vol. IV of ref 15. All compounds were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by silicon grease, and immediately placed in the low-temperature N$_2$ stream. The crystal data and refinement for **1** and **6** are described in Table 1 of the Supplementary Material. Notes on the solution of each structure and a detailed discussion of disorder for **6** is also provided therein. Table 2 (Supplementary Material) provides a summary of the crystal data from **3**, **4**, and **5**.

Results and Discussion

Structural Descriptions. (MesBPPh)$_3$ (1). The structure of **1** is illustrated in Figure 1 and consists of well-separated (MesBPPh)$_3$ molecules. There is a crystallographically imposed 3-fold rotation axis in the center of the (BP)$_3$ core. The three boron, three phosphorus, and six substituent carbons all lie in a plane as shown in Figure 2. The dihedral angles between the central (BP)$_3$ plane and the mesityl ring and the phenyl ring are 80.8° and 40.1°, respectively. The BP distance is 1.843 (3) Å, and the BPB and PBP angles are 124.5 (2)° and 114.9 (1)°, respectively. Other important distances are 1.802 (3) Å (phosphorus–carbon) and 1.567 (3) Å (boron–carbon).

(MesBPC$_6$H$_{11}$)$_3$ (2). The structure of **2** was reported in a preliminary communication and is illustrated in Figure 3. Like **1**, it has a planar $B_3P_3C_6$ core with equal BP distances of ca. 1.84 Å. The average PBP and BPB angles are 114.9 and 125.1°. The average PC and BC distances are 1.838 and 1.575 Å, respectively.

(MesBPMes)$_3$ (3). X-ray data showed that this compound crystallized as well-separated molecules containing a planar $B_3P_3C_6$ core. A partially occupied hexane molecule is also present in the lattice. The structure could not be refined satisfactorily due to the severe disorder between B and P atoms. This undoubtedly is due to the similar substituents (mesityl) on both the boron and phosphorus centers.

(MesBP-*t*-Bu)$_3$ (4). It is clear from the X-ray crystallographic study that **4** consists of well-separated (MesBP-*t*-Bu)$_3$ molecules. There is also a molecule of hexane in the asymmetric unit. The high rotational disorder of *tert*-butyl groups on phosphorus atoms is the only problem in the successful refinement of the structure. No reasonable model for this disorder could be obtained from the difference map.

(PhBPMes)$_3$ (5). This compound crystallized as yellow rod-shaped crystals. Suitable crystals for X-ray work were obtained with great difficulty from hexane after various attempts with different solvent systems and conditions. They tend to grow as clusters of rod-shaped crystals with severe twinning. The most interesting and convincing feature of the X-ray data is the very close similarity of its lattice constants to that of (MesBPPh)$_3$ (**1**). However, the absence of high-angle data, probably due to disorder, prevented satisfactory refinement of the structure.

(ThexylBPMes)$_2$·$^2/_3$Et$_2$O (6). The structure of **6** is illustrated in Figure 4. The (BP)$_2$ ring resides on a center of symmetry, and the molecules are well separated from each other in the crystal lattice. The important diphosphadiboretane structural unit refines smoothly. The BP distances are equivalent, with the average being 1.897 (6) Å. The boron center is planar and the PBP angle is 92.3 (3)°. The phosphorus center is pyramidal and the sum of the angles is 331.3°. The other important parameters concern BPB angle and the BC and PC distances, which are 87.7 (3)°, 1.577 (9) Å, and 1.835 (4) Å, respectively.

There is also a severely disordered Et$_2$O molecule with the oxygen atom on a 3-fold rotation axis. Only the oxygen atom was clearly identified on the basis of peak heights from the difference map and its subsequent refinement. Unfortunately, no other carbon atoms could be found; thus a suitable model for its disorder could not be obtained from the difference maps. Further details are provided in the Supplementary Material.

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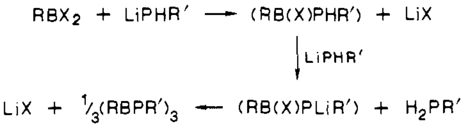
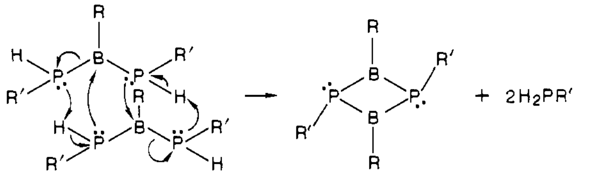
(15) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Scheme I



Scheme II



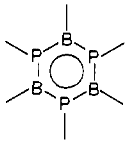
Discussion

Several new boraphosphabenzenes, the boron–phosphorus analogues of borazine, and a diphosphadiboretane, $(ThexylBPMes)_2$, are readily obtained in moderate yield from the reaction of $MesBBr_2$, $PhBCl_2$, or $ThexylBCl_2$ with 2 equiv of the lithium salts of various primary phosphines R′PHLi (R′ = Ph, Cy, Mes, *t*-Bu). The overall reaction for the formation of boraphosphabenzenes may be described by the equation

$$RBX_2 + 2LiPHR' \rightarrow \tfrac{1}{3}(RBPR')_3 + 2LiX + H_2PR'$$

This stoichiometry has been monitored by ^1H and ^{31}P NMR. The reaction between RBX_2 and 1 equiv of LiPHR′ does not afford RB(X)PHR′ but results in a lowered yield of $(RBPR')_3$. This suggests that the formation of $(RBPR')_3$ may be the result of the reaction sequence shown in Scheme I. An alternative mechanism involving the association of two $RB(PHR')_2$ molecules to give a species such as **6** with elimination of H_2PR' is also possible.[16] Bulkier substituents, particularly on boron, are expected to favor Scheme I over Scheme II. Indeed, the use of the (2,4,6-i-$Pr_3C_6H_2$ or Trip) groups has allowed the isolation of the species TripB(PHMes){PMesLi$(Et_2O)_2$}, which has been structurally characterized by X-ray diffraction in addition to ^{31}P and ^{11}B NMR. Similar species have been identified spectroscopically for the substituent pairs R/R′ = Mes/*t*-Bu and Trip/*t*-Bu. However, no such compound was detected for R/R′ = Mes/C_6H_{11} or Mes/Ph. These data indicate that two different mechanisms, which depend mainly on the size of the substituents, may operate. Further experiments are in progress in order to throw more light upon these possible mechanisms of formation.

Irrespective of the reaction pathway, compounds **1–5** are the first examples of a new class of ring compound containing a planar array of $B_3P_3C_6$ atoms similar to that of substituted borazines. The bonding in these compounds may be illustrated schematically as



representing delocalization of the phosphorus lone pairs. From the X-ray structures of **1** and **2** it is clear that all the BP distances are essentially equal and average 1.84 Å. In addition, this distance is significantly shorter than 1.96 Å in boron phosphide[17] and 1.93 Å in the trimer $(Me_2PBH_2)_3$.[18] In fact, the bond length is only slightly longer than the values of 1.82–1.83 Å seen for monomeric phosphinidene borates $[MesPBMes_2]^-$ (**7a**),[19] [Li$(Et_2O)_2$PRBMes$_2$][19] (**8a–c**) (R = Ph, C_6H_{11}, or Mes), and [Li$(Et_2O)_2$P(*t*-Bu)BR′$_2$][20] (**9a,b**) (R′ = Mes, Trip). All these species **7a–c**, **8a–c**, and **9a,b** have a planar phosphorus center and are thought to have a considerable amount of B–P double-bond character.

Table I. ^{31}P and ^{11}B NMR Data for Compounds **1–14**

compd	^{11}B	^{31}P	∑angle at P, deg	ref
$(MesBPPh)_3$ (**1**)	52.5	42.5	planar	this work
$(MesBPC_6H_{11})_3$ (**2**)	52.6	51.9	planar	this work
$(MesBPMes)_3$ (**3**)	49.6	40.4	planar	this work
(MesBP-*t*-Bu)$_3$ (**4**)	53.9	60.5	planar	this work
$(PhBPMes)_3$ (**5**)	50.2	14.5	planar	this work
$(ThexylBPMes)_2$ (**6**)	95.1	−70.7	331.3	this work
$[Mes_2BPMes]^-$ (**7a**)		91.3	planar	19
$[Mes_2BPPh]^-$ (**7b**)		103.6		19
$[Mes_2BPC_6H_{11}]^-$ (**7c**)		113.6		19
$[Mes_2BP(Mes)Li(Et_2O)_2]$ (**8a**)	63.7	55.5	planar	19
$[Mes_2BP(Ph)Li(Et_2O)_2]$ (**8b**)	65.4	73.1		19
$[Mes_2BP(C_6H_{11})Li(Et_2O)_2]$ (**8c**)	65.6	70.5	planar	19
[Mes$_2$BP(*t*-Bu)Li$(Et_2O)_2$] (**9a**)	62.5	104.3	planar	20
[Trip$_2$BP(*t*-Bu)Li$(Et_2O)_2$] (**9b**)	58.9	113.2	planar	20
$MesB(PPh_2)_2$ (**10**)	30.1	−0.01	332.7 (av)	22
$(Mes_2B)_2PPh$ (**11**)	47.8	60.1	planar	22
$(tmpBPMes)_2$ (**12**)			329.0	8
$(tmpBPAr)_2$ (**13**)		−90	333.7	7
$(tmpBPCEt_3)_2$ (**14**)	66.1	−20	329.2	9

Table II. ^1H NMR Data for **1–5** in C_6D_6 and Related Compounds[a]

$(RBPR')_3$	B–R		P–R′	
$(MesBPPh)_3$ (**1**)	o-CH_3	2.36	o-H	6.99
	p-CH_3	1.94	p-H	7.02
	m-H	6.58	m-H	6.56
$(MesBPC_6H_{11})_3$ (**2**)	o-CH_3	2.63	C_6H_{11}	0.68
	p-CH_3	2.17		0.84
	m-H	6.93		1.15
				1.42
				2.07
				2.32
$(MesBPMes)_3$ (**3**)	o-CH_3	2.52	o-CH_3	2.47
	p-CH_3	1.84	p-CH_3	1.72
	m-H	6.49	m-H	6.54
(MesBP-*t*-Bu)$_3$ (**4**)	o-CH_3	2.57		
	p-CH_3	2.14	$(CH_3)_3C$	1.11
	m-H	6.81		
$(PhBPMes)_3$ (**5**)	o-H	7.31	o-CH_3	2.45
	p-H	6.86	p-CH_3	1.93
	m-H	6.86	m-H	6.63
$BMesBr_2$	o-CH_3	2.76	C_6D_6	
	p-CH_3	2.66		
$PMesH_2$	o-CH_3	2.20	C_6D_6	
	p-CH_3	2.08		
$BMes_3$	o-CH_3	1.98	$(CDCl_3)$	
	p-CH_3	2.24		

[a] Values given in ppm [referenced to residual H (7.15 ppm) in C_6D_6].

The bond angles at boron and phosphorus in **1** and **2** deviate significantly from the ideal trigonal planar value of 120°. The BPB and PBP angles average 124.8 and 114.9°, respectively. Similar but smaller deviations are observed for borazine. For example, in $(HNBH)_3$, BNB = 121.1° and NBN = 117.7°.[21] The larger variations for boraphosphabenzenes may be a consequence of size difference between B and P.

It is also interesting to compare the structural parameters of **1** and **2** with the recently characterized compounds $MesB(PPh_2)_2$[22] (**10**) and $(Mes_2B)_2PPh$[22] (**11**). The BP distance of 1.84 Å for **1** is shorter than the average values of 1.89 and 1.87 Å seen for **10** and **11**. In **10**, two phosphorus centers, both of which are pyramidal, compete in donation to the boron p orbital whereas in the boraphosphabenzenes, the ratio is 1:1, making for more efficient delocalization. Thus, a longer BP distance is seen in **10**. Similarly, in **11** one phosphorus lone pair is delocalized over a three-atom BPB system, which also affords longer BP distances than in **1** or **2**.

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(16) Fritz, G.; Uhlmann, R. *Z. Anorg. Allg. Chem.* **1978**, *442*, 95.
(17) Perri, J. A.; La Placa, S.; Post, B. *Acta Crystallogr.* **1958**, *11*, 310.
(18) Hamilton, W. C. *Acta Crystallogr.* **1955**, *8*, 198.
(19) Bartlett, R. A.; Feng, X.; Power, P. P. *J. Am. Chem. Soc.* **1986**, *108*, 6817.
(20) Bartlett, R. A.; Power, P. P., unpublished results.
(21) Roberts, P. J.; Brauer, D. J.; Tsay, Y. H.; Krüger, C. *Acta Crystallogr., B* **1974**, *B30*, 2673.
(22) Bartlett, R. A.; Dias, H. V. R.; Power, P. P. *Inorg. Chem.*, submitted.

The ^{31}P, ^{11}B, and ^{1}H NMR spectroscopic data are summarized in Tables I and II. The positive ^{31}P chemical shifts for boraphosphabenzenes **1–5** are indicative of a lowered electron density at phosphorus as a result of delocalization of the electron density on to the boron. This is consistent with data for other related boron–phosphorus systems. It can also be seen from Table I that there is a rough correlation between the ^{31}P chemical shift and the degree of pyramidicity at phosphorus although there are exceptions. ^{11}B chemical shifts for these compounds average around 52 ppm and display little variation.

The diphosphadiboretane (ThexylBPMes)$_2$ is the only structurally characterized example of a dimer of a (RB≡PR′) unit that has no π-donor atoms attached to boron (other than phosphorus). The most closely related structurally characterized systems are (tmpBPMes)$_2$ (**12**), (tmpBPAr)$_2$ (**13**), and (tmpBPCEt$_3$)$_2$ (**14**). All these contain the 2,2,6,6-tetramethylpiperidino group on boron. The effect of a nitrogen substituent on the B–P bonding is seen clearly in their longer BP distances. The BP distances for **12**[8] (1.916 (3) Å), **13**[7] (1.96 (2) Å), and **14**[8] (1.916 (2) and 1.933 (2) Å) are all somewhat longer than the BP distance for **6** (1.897 (6) Å). The domination of the multiple bonding to boron by the nitrogen is also supported by short BN distances, which average near 1.4 Å in **12–14**. The BP bond distance can also be contrasted to those in phosphinoborane dimers such as [Ph$_2$BP(H)*t*-Bu]$_2$[23] (**15**), [B(PEt$_2$)$_3$]$_2$[24] (**16**), and (Ph$_2$PBI$_2$)$_2$[25] (**17**). The BP bond distances in these compounds average 2.026 (2) (**15**), 2.016 (6) (**16**), and 2.01 Å (**17**), which are considerably longer than the value seen for **6**. The main reason for the longer BP bonds is undoubtedly the four-coordinate nature of the B and P centers. A dramatic change is also observed in both the ^{31}P and ^{11}B NMR chemical shifts of **6** compared to the values seen in **1–5**. In the ^{31}P spectrum the singlet seen at −70 ppm is in sharp contrast to the positive values observed in **1–5**. Similarly, a more positive value (95.1 ppm) is seen in the ^{11}B spectrum of **6** whereas an average value of 52 ppm is seen for compounds **1–5**. These shifts point to increased electron density at phosphorus and decreased electron density at boron.

^{1}H NMR data for **1–5** and related compounds are given in Table II. The data provide confirmation of the structure and stoichiometry of the compounds. The data are also of interest in that it could provide evidence for the aromaticity of the B$_3$P$_3$ ring. Inspection of the chemical shifts of the ortho and para methyl groups of the BMes and PMes groups in compounds **1–5** shows that the resonance generally appear at a lower (0.1–0.4 ppm) chemical shift than the nonring compounds. In addition, the difference in shift between the ortho and para positions in **1–5** varies from 0.42 to 0.75 ppm whereas in normal mesityl derivatives the difference is less than 0.4 ppm and is usually between 0.3 and 0.1 ppm. In some compounds, for example in the silyl boranes,[26] the ortho methyl group even appears further downfield than the para group. In the case of **1–5** it can be argued that the ortho CH$_3$ of the mesityl substituents appears at somewhat lower field than expected due to the effects of the ring current increasing the magnetic field experienced by these protons. In our view the ^{1}H NMR data provide support, if not conclusive proof, for the aromatic character of the B$_3$P$_3$ ring.

The physical and chemical properties of phosphaborabenzenes also merit comment. All the compounds **1–5** have a high melting point (>250 °C) and do not decompose in sealed capillaries under N$_2$. Preliminary reactivity studies of **2** and **3** show that they react slowly with H$_2$O. The ^{31}P and ^{11}B signals of **3** are virtually undiminished in intensity even after 1 month in a "wet" THF solution.

Conclusion

The first boron–phosphorus analogues of borazine in addition to the first diphosphadiboretane, with no π substituents, have been synthesized and characterized both structurally and spectroscopically. The compounds are very stable thermally and in the case of **3** only very slowly attacked by moisture. The syntheses, in all cases, consist of just one step although preliminary data indicate that more than one mechanism of formation is possible.

Studies of the reactivity, coordination chemistry of these compounds, and the mechanistic aspects of the above synthetic approach are continuing. Studies on their heavier congeners are also in progress.

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Registry No. **1**, 117229-44-4; **2**, 111662-26-1; **3**, 117251-72-6; **4**, 117229-46-6; **5**, 117229-47-7; **6**, 117229-49-9; MesBBr$_2$, 87025-39-6; PhPHLi, 51918-34-4; PhPH$_2$, 638-21-1; MesPHz, 68357-98-2; *t*-BuPHLi, 67877-34-3; *t*-BuPH$_2$, 2501-94-2; MesPHLi, 89634-37-7; PhBCl$_2$, 873-51-8; ThexylBCl$_2$, 79200-82-1; PMesBr$_2$, 87437-12-5; PMesH$_2$, 68357-98-2; BMes$_3$, 7297-95-2.

Supplementary Material Available: Full tables of crystallographic data, summary of data collection and refinement, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates for **1** and **6**, explanatory notes as well as partial crystal data for compounds **3–5**, and diagrams for compounds **2–4** (20 pages). Ordering information is given on any current masthead page.

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[23] Bartlett, R. A.; Dias, H. V. R.; Power, P. P., unpublished results.

[24] Nöth, H. *Z. Anorg. Allg. Chem.* **1987**, *555*, 79.

[25] Bullen, G. J.; Mallinson, P. R. *J. Chem. Soc., Chem. Commun.* **1969**, 132.

[26] Dias, H. V. R.; Power, P. P., unpublished results.