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Synthesis and Spectroscopic and Structural Characterization of the Monomeric Diborylphosphine and Diphosphinoborane Compounds $PhP(BMes_2)_2$ and $MesB(PPh_2)_2$ ($Mes = 2,4,6-Me_3C_6H_2$)

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The synthesis and spectroscopic and first X-ray structural characterization of a diborylphosphine, $PhP(BMes_2)_2$ (**1**), and a diphosphinoborane, $MesB(PPh_2)_2$ (**2**), are described. The structure of **1** has a planar core that involves the phosphorus and two boron atoms and also the five substituent carbons. In addition, the B–P bond lengths are shortened, which suggests a close structural analogy between **1** and the allyl cation. In the case of **2**, although the boron remains planar, both phosphorus centers are pyramidal with slightly longer B–P bonds than in **1**. Both **1** and **2** are the first examples of their respective classes of compound to be well characterized. Crystal data with Mo Kα radiation (λ = 0.71069 Å) at 130 K are as follows. **1**: a = 14.302 (4) Å, b = 15.701 (3) Å, c = 16.601 (6) Å, β = 109.61 (2)°; monoclinic, space group $C2/c$, Z = 4, R = 0.059. **2**: a = 7.815 (2) Å, b = 8.723 (2) Å, c = 40.147 (10) Å, β = 94.90 (2)°; monoclinic, space group $P2_1/n$, Z = 4, R = 0.041. A listing of available ^{11}B and ^{31}P NMR data on compounds involving triply connected boron and phosphorus centers is also provided and discussed in the context of the data for **1** and **2**.

Introduction

Despite the widespread knowledge of the structure, bonding, and reactivity of boron–nitrogen compounds[1], information concerning their boron–phosphorus analogues remains sparse.[2] In addition, the isoelectronic relationship between the B–N and C–C pairs has provided much impetus for the investigation of the boron–nitrogen species. However, the absence of well-defined, multiply bonded, heavier main-group analogues has precluded similar comparisons for the pairs such as B=P and C=Si. Structural information on stable silenes such as $(Me_3Si)_2Si{=}C(OSiMe_3)$(adamantyl) and $Me_2Si{=}C(SiMe_3)(SiMe\text{-}t\text{-}Bu_2)$ has become available only recently.[3,4] Similarly, spectroscopic and structural data on their boron–phosphorus analogues, the monomeric phosphinoboranes, is equally scarce,[5,6] although phosphinoboranes ($R_2PBR'_2$; R, R′ = alkyl or aryl group) have been known for a number of years and they are usually found as cyclic oligomers in the crystal.[7] In addition, cryoscopic measurements by Coates and Livingstone[8] have shown that, in dilute (~0.5 wt %) solutions, some species such as Ph_2BPEt_2 and $(4\text{-}BrC_6H_4)_2BPEt_2$ mainly exist as monomers. It is therefore surprising to note that the first crystal structures of the monomeric phosphinoborane Mes_2BPPh_2[5] and tmp(Cl)BP(H)Mes[6,9] were not published until recently. Similarly bifunctional phosphinoboranes exemplified by the general formulas $RP(BR'_2)_2$ and $RB(PR'_2)_2$ have been known since 1961,[8] yet other than infrared and cryoscopic data, there is little further information available.

We have investigated some of these multifunctional boron–phosphorus compounds and have shown that the reaction between 2 equiv of $LiHPC_6H_{11}$ and $MesBBr_2$ gives $(MesBPC_6H_{11})_3$, the first boraphosphabenzene,[10] rather than the expected $MesB(PHC_6H_{11})_2$ product. We now report the synthesis, X-ray crystal structures, and ^{11}B and ^{31}P NMR data for the compounds $PhP(BMes_2)_2$ and $MesB(PPh_2)_2$. Available NMR data of some of the related compounds are also reported.

Table I. Crystallographic Data for $PhP(BMes_2)_2$ (**1**) and $MesB(PPh_2)_2$ (**2**)

	$PhP(BMes_2)_2$	$MesB(PPh_2)_2$
chem formula	$C_{42}H_{49}B_2P$	$C_{33}H_{31}BP_2$
a, Å	14.302 (4)	7.815 (2)
b, Å	15.701 (3)	8.723 (2)
c, Å	16.601 (6)	40.147 (10)
β, deg	109.61 (2)	94.90 (2)
V, Å^3	3513 (2)	2727 (1)
Z	4	4
fw	606.50	500.36
space group (No.)	$C2/c$ (15)	$P2_1/n$ (14)
T, K	130	130
λ, Å	0.71069	0.71069
ρ(calc), g cm^{-3}	1.15	1.22
μ, cm^{-1}	1.02	1.74
transmission coeff	0.96–1.0	0.83–0.89
$R(F)$	0.059	0.041
$R_w(F)$	0.064	0.042

Experimental Section

All manipulations were carried out under N_2 by standard Schlenk techniques. Solvents were freshly distilled under N_2 over Na/K alloy-benzophenone ketyl and degassed twice immediately before use. ^{31}P and ^{11}B spectra were obtained in C_6D_6/THF solutions by using a Nicolet NT-200 spectrometer operating near 81 and 64 MHz, respectively. Mes_2BF[11] and $MesBBr_2$[12] were synthesized by published procedures. Ph_2PH and $PhPH_2$ were prepared from the $LiAlH_4$ reduction of their respective chlorides. n-BuLi (1.6 M in hexane) was purchased from Aldrich and used as received. ^{11}B and ^{31}P chemical shifts were referenced to external $BF_3{\cdot}Et_2O$ and H_3PO_4 standards.

Synthesis of Compounds 1 and 2. $PhP(BMes_2)_2$ (1). $Mes_2BPPhLi$ was prepared in situ by treating Mes_2BF (2.68 g, 10 mmol) in Et_2O (30 mL) with PhPHLi (1 equiv) in THF (20 mL) at room temperature for 3 h, followed by the addition of n-BuLi (6.3 mL, 1.6 M in hexane) at 0 °C. This mixture was stirred for 30 min; solid Mes_2BF (2.6 g) was then added slowly, and the resultant mixture was stirred for 30 min at room temperature. Then the reaction mixture was refluxed for 3 h and cooled, and the solvents were removed under reduced pressure. The residue was extracted into hexane, and the mixture was filtered, concentrated, and cooled at −20 °C to obtain yellow crystals of **1** in 42% yield (2.5 g): ^{31}P NMR δ 60.09; ^{11}B NMR δ = 47.8.

$MesB(PPh_2)_2$ (2). $MesBBr_2$ (1.9 g, 6.5 mmol) in hexane (20 mL) was added dropwise at −10 °C to Ph_2PLi (from Ph_2PH, 2.44 g, 13 mmol, and n-BuLi in hexane, 1.6 M, 8.1 mL) in Et_2O (20 mL). The reaction mixture was stirred overnight at room temperature, and volatiles were removed under vacuum. The residue was extracted into hexane, and the mixture was filtered and cooled at −20 °C. Pale yellow crystals of **2** were obtained in 31% yield (1.02 g): ^{31}P NMR δ −0.01; ^{11}B NMR δ 30.1.

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	U^a
		Compound **1**		
P	0	196 (1)	2500	32 (1)
B	1143 (2)	691 (2)	3267 (2)	25 (1)
C(1)	1237 (2)	1690 (2)	3313 (2)	26 (1)
C(2)	1275 (2)	2095 (2)	4086 (2)	27 (1)
C(3)	1319 (2)	2976 (2)	4150 (2)	32 (1)
C(4)	1350 (2)	3482 (2)	3481 (2)	34 (1)
C(5)	1346 (2)	3088 (2)	2735 (2)	34 (1)
C(6)	1279 (2)	2210 (2)	2634 (2)	29 (1)
C(7)	1223 (2)	1589 (2)	4842 (2)	31 (1)
C(8)	1391 (3)	4440 (2)	3567 (2)	51 (1)
C(9)	1283 (2)	1856 (2)	1788 (2)	35 (1)
C(10)	1968 (2)	60 (2)	3844 (2)	24 (1)
C(11)	1790 (2)	−558 (2)	4385 (2)	27 (1)
C(12)	2533 (2)	−1124 (2)	4826 (2)	30 (1)
C(13)	3470 (2)	−1105 (2)	4757 (2)	31 (1)
C(14)	3652 (2)	−487 (2)	4240 (2)	32 (1)
C(15)	2938 (2)	98 (2)	3791 (2)	28 (1)
C(16)	823 (2)	−628 (2)	4557 (2)	35 (1)
C(17)	4262 (2)	−1720 (2)	5242 (2)	42 (1)
C(18)	3216 (2)	749 (2)	3248 (2)	38 (1)
C(19)	0	−955 (2)	2500	32 (1)
C(20)	812 (2)	−1403 (2)	2427 (2)	38 (1)
C(21)	804 (3)	−2286 (2)	2432 (2)	49 (1)
C(22)	0	−2729 (3)	2500	54 (2)
		Compound **2**		
P(1)	5832 (1)	3014 (1)	4111 (1)	19 (1)
P(2)	2373 (1)	4051 (1)	3649 (1)	19 (1)
B	4646 (3)	3330 (3)	3683 (1)	18 (1)
C(1)	5637 (2)	2954 (2)	3369 (1)	18 (1)
C(2)	6704 (2)	4079 (2)	3244 (1)	20 (1)
C(3)	7748 (3)	3700 (3)	2993 (1)	24 (1)
C(4)	7762 (3)	2227 (3)	2858 (1)	25 (1)
C(5)	6678 (3)	1137 (3)	2979 (1)	24 (1)
C(6)	5620 (3)	1475 (2)	3231 (1)	21 (1)
C(7)	6759 (3)	5684 (2)	3388 (1)	28 (1)
C(8)	8905 (3)	1835 (3)	2586 (1)	41 (1)
C(9)	4490 (3)	238 (3)	3358 (1)	29 (1)
C(10)	7100 (2)	1269 (2)	4071 (1)	19 (1)
C(11)	8405 (2)	1267 (2)	3851 (1)	20 (1)
C(12)	9334 (3)	−53 (2)	3803 (1)	23 (1)
C(13)	9014 (3)	−1383 (3)	3974 (1)	25 (1)
C(14)	7765 (3)	−1384 (3)	4199 (1)	25 (1)
C(15)	6825 (3)	−67 (2)	4249 (1)	23 (1)
C(16)	4284 (2)	2493 (2)	4409 (1)	18 (1)
C(17)	4470 (3)	3151 (3)	4727 (1)	23 (1)
C(18)	3337 (3)	2785 (3)	4963 (1)	29 (1)
C(19)	2017 (3)	1762 (3)	4886 (1)	27 (1)
C(20)	1804 (3)	1104 (2)	4571 (1)	24 (1)
C(21)	2939 (3)	1469 (2)	4334 (1)	21 (1)
C(22)	2095 (2)	5208 (2)	4020 (1)	19 (1)
C(23)	3205 (3)	6407 (2)	4123 (1)	23 (1)
C(24)	3019 (3)	7178 (3)	4418 (1)	27 (1)
C(25)	1732 (3)	6755 (3)	4619 (1)	28 (1)
C(26)	611 (3)	5588 (3)	4518 (1)	25 (1)
C(27)	782 (3)	4823 (2)	4219 (1)	21 (1)
C(28)	2031 (2)	5306 (2)	3287 (1)	20 (1)
C(29)	2242 (3)	4709 (3)	2970 (1)	25 (1)
C(30)	1827 (3)	5578 (3)	2684 (1)	28 (1)
C(31)	1181 (3)	7044 (3)	2709 (1)	29 (1)
C(32)	974 (3)	7655 (3)	3021 (1)	28 (1)
C(33)	1420 (3)	6804 (2)	3308 (1)	24 (1)

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

Table III. Selected Bond Distances (Å) and Angles (deg)

	Compound **1**		
P–B	1.871 (2)	B–C(1)	1.574 (4)
P–B′	1.871 (2)	B–C(10)	1.591 (3)
P–C(19)	1.807 (4)		
B–P–B′	131.0 (2)	P–B–C(1)	119.2 (2)
B–P–C(19)	114.5 (1)	P–B–C(10)	117.0 (2)
B′–P–C(19)	114.5 (1)	C(1)–B–C(10)	123.9 (2)
	Compound **2**		
P(1)–B	1.901 (2)	P(2)–C(22)	1.825 (2)
P(2)–B	1.879 (2)	P(2)–C(28)	1.823 (2)
P(1)–C(10)	1.831 (2)	B–C(1)	1.569 (3)
P(1)–C(16)	1.831 (2)		
B–P(1)–C(10)	105.5 (1)	B–P(2)–C(28)	109.4 (1)
B–P(1)–C(16)	109.2 (1)	C(22)–P(2)–C(28)	107.4 (1)
C(10)–P(1)–C(16)	104.1 (1)	P(1)–B–P(2)	119.9 (1)
B–P(2)–C(22)	107.7 (1)	P(1)–B–C(1)	117.4 (1)
B–P(2)–C(22)	107.7 (1)	P(2)–B–C(1)	122.7 (1)

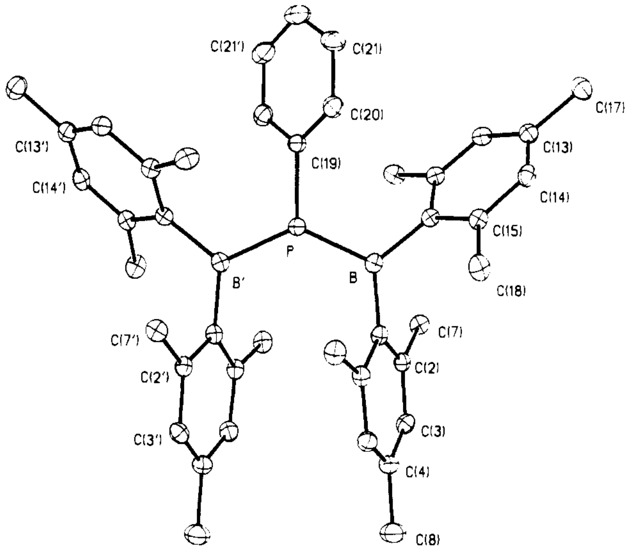

Figure 1. Computer-generated thermal ellipsoid plot of **1**. Hydrogen atoms are omitted for clarity.

X-ray Crystallographic Studies

X-ray data were collected by using a Syntex P2_1 diffractometer equipped with a locally modified Syntex LT-1 device. Calculations were carried out on a Data General Eclipse computer using the SHELXTL program system, Version 5. The atom form factors, including anomalous scattering, were from ref 13.

Crystals of both **1** and **2** were transferred from the Schlenk tube under N_2 and immediately covered with a layer of hydrocarbon oil. A single crystal was selected, attached to a glass fiber, and immediatley place in the low-temperature N_2 stream. Some details of the data collection and refinement are given in Table I, and further details are provided in the supplementary material. Both structures were solved by using direct methods. Hydrogen atoms were included at calculated positions by using a riding model with C–H of 0.96 Å and $U_{iso}(H) = 1.2U^*_{iso}(C)$, where U^*_{iso} is the equivalent isotropic thermal parameter. All nonhydrogen atoms were refined anisotropically. An absorption correction was applied in the refinement of **1** by the use of the program XABS.[14] Atom coordinates and isotropic thermal parameters are given in Table II. Selected bond distances and angles are provided in Table III.

Results and Discussion

Structural Descriptions. PhP(BMes$_2$)$_2$ (1). The structure of **1** as illustrated in Figure 1 consists of well-separated molecules of PhP(BMes$_2$)$_2$. There is a crystallographically imposed 2-fold rotation axis along the P–C(19) bond, implying a planar phosphorus center. The boron center is also planar, and there is only a very small dihedral angle between the BC(1)C(10) and PBC(19) planes. In effect, the extended core of the molecule involving PC(19)BC(1)C(16)B′C(1)′C(16)′ is very close to planarity. There are only minor deviations from purely trigonal values in the angles at boron. At phosphorus, however, the BPB angle is quite wide at 131.0 (2)°. The dihedral angle for the Ph ring is 50.1°, and the corresponding angles for the C(1) and C(10) mesityl rings

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Table IV. ^{11}B and ^{31}P NMR Data for Compounds Involving Bonding between Three-Coordinate Boron and Three-Coordinate Phosphorus

compd	$\delta(^{11}B)$	$\delta(^{31}P)$	$\sum$angles at P, deg	ref
$PhP(BMes_2)_2$ (**1**)	47.8	60.1	planar	this work
$MesB(PPh_2)_2$ (**2**)	30.1	−0.01	av 322.7	this work
Ph_2PBMes_2 (**3**)	51.7	30.2	339.4	5
$Et_3C(H)PB(Cl)tmp$ (**4**)	46.1	−88.2	(probably pyramidal)	16
$Ar(H)PB(Cl)tmp$ (**5**)	47.6	−98.7	307.1	6, 24
Ar(Me)PB(*t*-Bu)tmp (**6**)	58.0	−14.6	(probably pyramidal)	24
$Ar(Me_3Si)PB$(*t*-Bu)tmp (**7**)	62.0	−23.6	(probably pyramidal)	24
$Li(Et_2O)_2P(Ph)BMes_2$ (**8**)	65.4	73.1	planar	23
$Li(Et_2O)_2P(C_6H_{11})BMes_2$ (**9**)	65.6	70.05	planar	23
$Li(Et_2O)_2P(Mes)BMes_2$ (**10**)	63.7	55.5	planar	23
$Li(Et_2O)_2P(SiMe_3)BMes_2$ (**11**)	71.6	−49.2	planar	22
LiP(Ar)B(Me)tmp (**12**)		72	unknown	15
LiP(Ar)B(*t*-Bu)tmp (**13**)		85.87	unknown	15
$(tmpBPAr)_2$ (**14**)		−90	333.7	15
$[MesPB(thexyl)]_2$ (**15**)	95.1	−70.7	331.3	22
$(tmpBPCEt_3)_2$ (**16**)	66.1	−20	329.2	16
$(Me_2NBPSiMe_3)_2$ (**17**)		153	unknown	19
$(PhPBMes)_3$ (**18**)	52.5	42.5	planar	22
$(C_6H_{11}PBMes)_3$ (**19**)	52.6	51.9	planar	18
$(MesPBPh)_3$ (**20**)	50.2	14.5	planar	22
$(MesPBMes)_3$ (**21**)	49.6	40.4	planar	22
$(t\text{-}BuPBMes)_3$ (**22**)	53.9	60.5	planar	22
$\mathrm{Ph\overline{PB(N\text{-}\mathit{i}\text{-}Pr_2)CHCHB}(N\text{-}\mathit{i}\text{-}Pr_2)}$ (**23**)	47.7	−124.6	295.9	17

are 65.1 and 58.5°. The mean B–C distance is close to 1.583 Å, which is similar to that reported in other compounds having the $-BMes_2$ group. The more important P–B and P–C(19) lengths are 1.871 (2) and 1.807 (4) Å.

$MesB(PPh_2)_2$ (2). The strucutre of **2** is illustrated in Figure 2, which also includes a different perspective of the more important core atoms. Complex **2** consists of well-separated $MesB(PPh_2)_2$ molecules that have no imposed symmetry restrictions. The boron center is planar with only small deviations from 120° in its angles. Both phosphorus atoms are pyramidal. The sum of the P(1) angles is 318.8°, and the angles of P(2) total 324.5°. The respective B–P(1) and B–P(2) bonds are 1.901 (2) and 1.879 (2) Å in length. The mesityl (C(1)) ring is almost perpendicular to the plane C(1)BP(1)P(2), forming a dihedral angle of 87.5°.

Discussion

Compounds **1** and **2** are the first diborylphosphine and diphosphinoborane compounds to be characterized by X-ray diffraction and ^{11}B and ^{31}P NMR spectroscopy. Related compounds that have recently been structurally reported all involve cyclic species: $(tmpBPAr)_2$,[6,15] $(tmpBPCEt_3)_2$,[16] $\mathrm{Ph\overline{P\text{–}B(N\text{-}\mathit{i}\text{-}Pr_2)\text{-}CHCHB}N\text{-}\mathit{i}\text{-}Pr_2}$,[17] $(MesBPC_6H_{11})_3$,[10] $\{B(PEt_2)_3\}_2$.[18] In addition, both **1** and **2** are very rare instances of molecules in their respective classes. Prior examples are $PhP(BPh_2)_2$ and $PhB(PPh_2)_2$, which were characterized by elemental analysis and cryoscopy.[8] The scarcity of ^{11}B and ^{31}P NMR spectroscopic data on compounds involving bonding between three-coordinate boron and three-coordinate phosphorus may be gauged from Table IV, which lists the currently available data. A number of other compounds with triply conected B and P have been reported, for example $(Me_3SiPBNMe_2)_2$.[19] However, both the ^{11}B and ^{31}P NMR data are not always available for each compound. Although the current data are insufficient to make very many broad generalizations, it is obvious that the ^{31}P chemical shifts are very sensitive to the degree of pyramidality at phosphorus and there is fairly good correlation between these two parameters. Thus, the pyramidal phosphorus centers in **4**–**7**, **14**, **16**, and **23** (in which the nitrogen rather than the phosphorus lone pair is involved in bonding to boron) all possess negative ^{31}P δ values. The somewhat less pyramidal phosphorus centers in **2** and **3** have more positive shifts whereas the planar compounds **1**, **8**–**10**, **12**, and **18**–**22** all have more positive ^{31}P δ values, suggesting more deshielded phosphorus nuclei. Presumably, this is due to the involvement of the phosphorus lone pair in π-bonding to boron, which reduces the electron density at phosphorus. The ^{11}B chemical shifts display much less variation. This is rather more expected, since in all compounds the boron centers are invariably planar. The vast majority of the ^{11}B shifts for these compounds are within 10 ppm of δ 55.

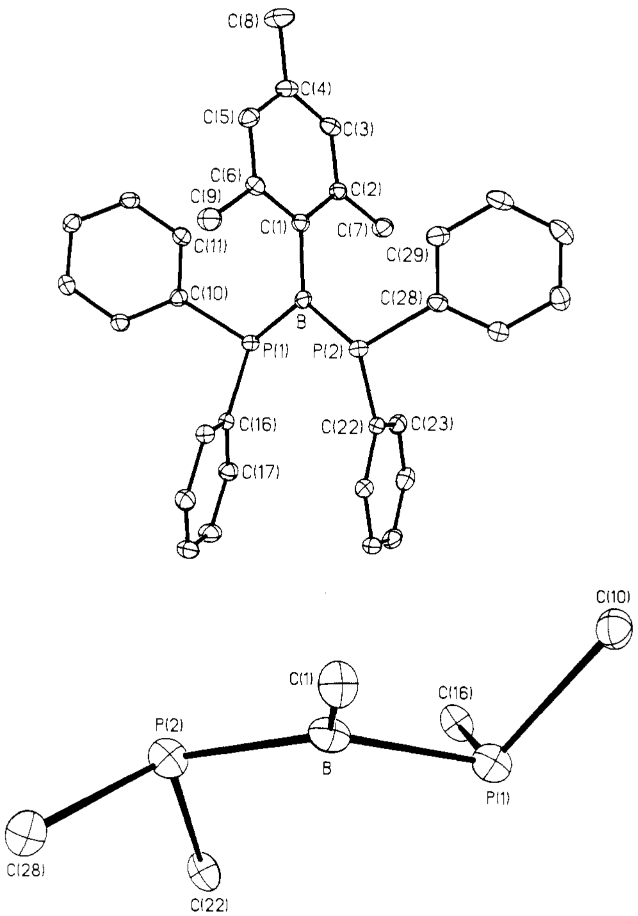

Figure 2. Top: Computer-generated thermal ellipsoid plot of **2**. Hydrogen atoms are omitted for clarity. Bottom: View of the core atoms of **2**.

The structural details of **1** and **2** merit comment. The most conspicuous feature of the structure of **1** is the planar nature of

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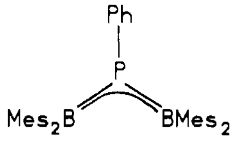
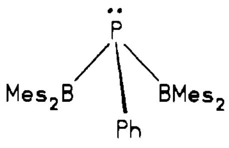
the phosphorus center. Planar tricoordinate phosphorus is a common feature of the structure of numerous metal phosphinidenes of the type $RP[M(CO)_n]_2$.[20] The phosphorus in **1** differs fundamentally from these because its valence shell possesses four electron pairs, with three used in σ-bonds to the borons and the carbon and the remaining pair available for π-donation to the empty boron p orbitals. In the metal phosphinidenes the RP moiety involves three electron pairs and behaves as a σ-donor to two metal carbonyl fragments and in addition is σ-bonded to an R group. The remaining phosphorus orbital behaves as a π-acceptor from the metal d orbitals. Thus, the bonding in **1** may be represented schematically as I rather than II, which involves no π-bonding. The planarity in **1** also extends to the C(1) and C(10) atoms in spite of the large size of the mesityl groups. This feature of the structure provides further evidence of π-bonding in the B–P–B moiety, which is maximized by having all three p orbitals parallel to each other even at the expense of considerably greater steric congestion. In effect, the structure of **1** suggests a considerable resemblance between it and a coresponding allyl cation, which has a pair of electrons in a strongly bonding π orbital, as depicted schematically by I.



I



II

The planar nature of the boron atom is preserved in the structure of $MesB(PPh_2)_2$ (**2**). However, in this case, the planarity does not extend to the phosphorus centers, which are both pyramidal. It is interesting to note that there is close correlation betwen the degree of pyramidality at each phosphorus and the B–P bond lengths. The longer B–P distance is found with the more pyramidal phosphorus center. This is of course consistent with reduced p–p overlap, which is less efficient in the case of the less planar center. It is also notable that although the phosphorus centers are clearly pyramidal, they are flatter than those in common phosphorus compounds such as PPh_3 ($\sum P$ angles = 310°).[21] Thus, both the shorter B–P distances in **2** and phosphorus angles suggest a reduced p-p π-interaction between boron and phosphorus. However, this is less than that seen in Mes_2BPPh_2, which has a B–P distance of 1.859 Å and $\sum P$ angles = 339.4°.[5] Just as an analogy can be drawn between **1** and the allyl cation, it is possible to compare **2** with the allyl anion. In this case, however, the structural analogy is not quite as clear-cut owing to the pyramidality of the phosphorus centers. However, it is notable that theoretical calculations on the allyl anion indicate that there is essentially no difference in energy between the planar and pyramidal forms.[25] Thus, for **1** it is possible to argue that the π-bonding orbital, which is delocalized over the three-atom system BPB, is very strongly bonding and thus very stable so that the planar system is preferred over all other canonical forms. However, to preserve a planar structure in **2**, the extra two electrons would have to be accommodated in a nonbonding orbital. This configuration apparently offers only a marginal energy advantage compared to a nondelocalized system so that the structure seen in **2** with pyramidal phosphorus atoms and much poorer delocalization results.

The structures of both **1** and **2** may also be compared with some recently reported cyclic B–P compounds. Owing to its planar nature, **1** may be most readily compared to the cyclic phosphaborabenzene $(MesBPC_6H_{11})_3$.[10] The main structural differences involve a somewhat wider BPB angle in **1** (131° compared to 124°) and also a slightly longer B–P bond (1.871 (2) Å compared to 1.84 Å). The wider angle in **1** is to be expected owing to the less restricted nature of its structure and also the presence of two bulky $-BMes_2$ groups on the phosphorus atom. In addition, the longer bond in **1** may also be a consequence of the greater steric crowding in comparison to the case of $(MesBPC_6H_{11})_3$. Similarly, the compound **2** may be compared to other systems involving the PBP moiety. Currently, these are restricted to cyclic systems such as $(tmpBPAr)_2$,[6,15] $(tmpBPCEt_3)_2$,[16] $[B(PEt_2)_3]_2$,[18] and the B–P benzene analogue above. The B–P bonds in **2** are shorter than those in all these cases except the B–P benzene compound. This is because the cyclic species either (a) contain tmp bonded to boron, which (due to the lone pair on N) reduces any multiple B–P character, or (b) involve four-coordinate boron as in $[B(PEt_2)_3]_2$, which has the effect of lengthening the B–P bond. Studies on **1** and **2** and related systems involving other substituents as well as their heavier congeners are continuing.

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Supplementary Material Available: Tables S1, S1a, S1b, S2a, and S2b, giving details of crystallographic data and summary of data collection and refinement, bond distances, and bond angles, and Tables S3a, S4a, S3b, and S4b, giving anisotropic thermal parameters and hydrogen coordinates (9 pages); listings of structure factors (44 pages). Ordering information is given on any current masthead page.

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