Syntheses and Molecular Structures of an Isoelectronic Series of (2-Hetero-)1,3-Diphosphabenzenes

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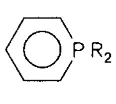
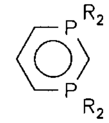
Syntheses, NMR spectra, and X-ray molecular structures of three (2-hetero-)1,3-diphosphabenzenes are reported which constitute an isoelectronic triade of compounds with BH_2, CH, and N bridging units between the two phosphorus atoms. The remaining three carbon atoms of the rings are part of a 2-methallylic system. The 2-borataheterocycle **3** has been prepared by the reaction of $CH_2{=}C(CH_2PPh_2)_2$ (**1**) with Me_2S-BH_2Br to give an intermediate **2** still containing the exocyclic olefinic bond. Treatment of **2** with a base, deprotonation of one ring CH_2 group, and proton migration from the other one to the olefinic CH_2 group afford the 5-methyl-1λ^5-phospha-3-phosphonia-2-boratabenzene **3**. The PBP unit is tilted by 144.0(2)° against the planar C_3P_2 part of the ring. A heterocyclic precursor **4** for the carbon analog is generated from **1** and CH_2I_2, which on reaction with a strong base yields the diphosphabenzene **5** with a fully planar ring skeleton. For the synthesis of the aza analog **7**, $CH_2{=}C(CH_2Cl)_2$ is treated with $HN(PPh_2)_2$ to give the precursor **6**, which can be deprotonatad at nitrogen and carbon with a base. In the crystals of **7**, two independent molecules of very similar structure are present. The molecules show planar heterocycles.

Phosphabenzenes (phosphinines) **A** containing λ^5-P atoms, discovered as early as 1963[1,2], continue to attract considerable interest both from a synthetic and theoretical point of view[3]. The chemistry of mono-λ^5-phosphabenzenes in particular has developed to an important area of heterocyclic chemistry[4,5]. However, though the advent of 1λ^5,3λ^5-diphosphabenzenes **B** also dates back to 1963[6], work in this area was only resumed many years later by Fluck et al. who were able to describe an improved synthesis of 1,3-diphosphabenzenes, at least for certain substitution patterns[7].



A



B

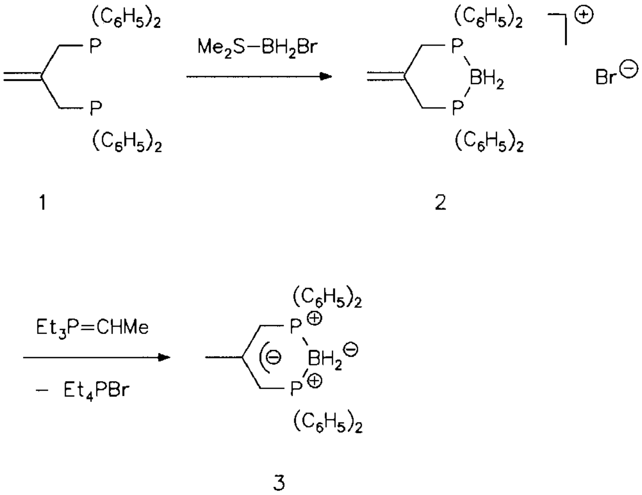
5-Methyl-1,1,3,3-tetraphenyl-1λ^5,3λ^5-diphosphabenzene is a prototype of this class of compounds, which has become available only more recently from studies of the chemistry of the rearrangements of cyclic multi-ylides. In one of these processes a proton transfer from an endocyclic to an exocyclic methylene group leads to the formation of a methallyl moiety in conjugation with the semi-ylide function $P{=}CH-P$, as already presented in a recent preliminary communication from our laboratory[9]. We now report on details of this work and new results on 2-aza-1λ^5,3λ^5-diphospha and 1λ^5-phospha-3-phosphonia-2-borata analogs, which together with the corresponding 1λ^5,3λ^5-diphosphabenzene constitute a triade of isoelectronic/isosteric species.

Preparation, Spectroscopic Data, and Molecular Structure of the 1λ^5-Phospha-3-phosphonia-2-boratobenzene 3

Cyclization of 1,1-Bis[(diphenylphosphino)methyl]ethene (**1**) with Me_2S-BH_2Br in toluene affords the 1,3-diphosphonia-2-borata salt **2**[8] in good yields.

When this product is treated with one equivalent of triethyl(ethylidene)phosphorane (as a transylidating agent) at −78°C a rearrangement involving proton abstraction and migration occurs (Scheme 1) to give the title compound **3** again in high yields. The compound **3** melts with decomposition at 116°C and shows an intense yellow color.

Scheme 1



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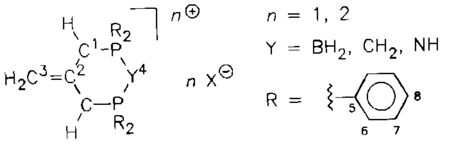
The NMR spectra (Table 2) are in full agreement with the proposed symmetrical structure in solution. The ^{31}P-NMR spectrum of a THF solution shows a broad line shifted to higher field as compared to that of compound **2** (Table 1), indicating equivalent phosphorus atoms attached to a common boron center which are more strongly shielded due to the neighboring allylic π-system. The ^{1}H-decoupled ^{11}B-NMR spectrum exhibits a broad triplet with the coupling constant ^{1}J(PB) = 90 Hz. The chemical shift is nearly the same as the one found for **2** and the cyclic 1,1,3,3-tetraphenyl-1,3-diphosphonia-2-boratacyclohexane iodide[10], demonstrating that no significant ring strain affects the $[Ph_2P-BH_2-PPh_2]^{\oplus}$ part of the heterocycle. Further support is provided by the ^{1}H-NMR and ^{1}H-decoupled ^{13}C-NMR spectra (Table 2), which show signals of equivalent methine and phenyl groups. The CH_3 resonances are 1:2:1 triplets.

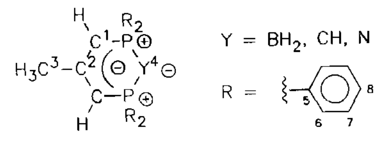
Table 1. NMR parameters of compounds **2**, **4**, **6** at 300 K; solvents: $[D_4]CH_3OH$ [^{1}H,^{13}C (**6**)], $[D_6]$DMSO [^{1}H,^{13}C,^{31}P (**4**); ^{31}P (**6**)], $CDCl_3$ [^{1}H,^{11}B,^{13}C,^{31}P (**2**)]



		δ/ppm					^{n}J/Hz, n = 1 - 4		
		2	**4**	**6**			**2**	**4**	**6**
^{31}P	P	3.6	13.2	28.4	n=1	PC^1	39.7	-	58.6
						PC^4		40.0	
						PC^5	67.1	-	109.3
^{13}C	C^1	31.6	26.9	35.0		C^1H^1	-	-	135.3
	C^2	130.5	128.0	131.4		C^3H^3			160.0
	C^3	124.3	126.3	122.2	n=2	PC^2	6.1	-	9.8
	C^4		13.3			PC^6	-	5.7	-
	C^5	123.7	117.4	128.7	n=3	PC^3	-	10.3	9.5
	C^6	132.1	132.6	132.3		PC^7	-	6.9	-
	C^7	129.1	129.9	130.5	n=4	PC^5	4.6	-	-
	C^8	132.3	135.4	134.7					
^{11}B	B	-54.9							
^{1}H	H^1	4.0	4.71	3.86	n=2	PH^1	17.1	15.3	14.7
	H^3	5.4	5.97	5.38		PH^4		15.3	
	H^4		5.72		n=4	PH^3	3.1	-	3.4
	H^6	7.3 -	7.6 -	7.8 - 7.9					
	$H^{7/8}$	7.7	8.0	7.3 - 7.7					

Compound **3** crystallizes in the monoclinic space group $P2_1/n$ (no. 14) with one complete molecule in the asymmetric unit. The molecular structure is based on a six-membered ring which adopts a half-chair conformation (Figure 1). The idealized mirror symmetry (C_s) of the ring is reduced to C_1 symmetry by the orientation of the four phenyl rings [angles between normals to planes: ring(C11) and ring(C12) = 94.0°, ring(C21) and ring(C22) = 78.8°] and the H atoms of the exocyclic methyl group. The methallylic part of the ring system is almost planar (with a maximum deviation from planarity for atom C1 of 0.05 Å). Accordingly, the sum of the angles at C2 is exactly 360.0(2)°. The inner angle at C2 [129.0(2)°] is significantly expanded from 120°, the outer ones are compressed [114.5(2), 116.5(2)°]. The ring angles C(phenyl)−P−C(phenyl) at the two P centers are compressed to an average value of 103.1(1)° (Table 3).

Table 2. NMR parameters of compounds **3**, **5**, **7** at 300 K; solvents: $[D_6]$benzene [^{1}H,^{13}C,^{31}P (**5**)], $[D_8]$THF [^{1}H,^{11}B,^{13}C,^{31}P (**3**); ^{1}H,^{13}C,^{31}P (**7**)]



		δ/ppm					^{n}J/Hz, n = 1 - 4		
		3	**5**	**7**			**3**	**5**	**7**
^{31}P	P	-5.2	7.1	20.1	n=1	PB	90		
^{13}C	C^1	52.7	51.8	53.3	n=1	PC^1	85.4	86.2	111.7
	C^2	164.5	159.5	163.7		PC^4		109.1	
	C^3	31.1	30.5	30.0		PC^5	67.1	-	106.0
	C^4		3.0			C^1H^1	163.2	-	159.8
	C^5	134.8	139.3	138.4		C^3H^3	126.0	-	126.0
	C^6	132.5	131.2	128.6	n=2	PC^2	12.0	6.9	6.9
	C^7	128.8	-	131.2		C^5B	4.58		
	C^8	130.5	129.7	130.8		PC^6	9.9	5.3	12.2
						C^2H^1	22.8	-	-
						C^2H^3	6.0	-	-
					n=3	PC^1	-	-	12.6
						PC^3	18.0	17.9	17.1
						PC^7	10.68	-	10.68
						C^3H^1	5.06	-	-
					n=4	PC^8	-	-	3.06
^{11}B	B	-54.8			n=1	PB	90		
^{1}H	H^1	3.43	3.40	3.38	n=2	PH^1	-	-	25.0
	H^3	2.36	2.26	2.10	n=4	PH^3	1.22	1.5	1.5
	H^4		1.15						
	H^6	6.88-6.96	7.0-	7.27-7.38					
	$H^{7/8}$	7.6-7.7	7.7	7.6-7.7					

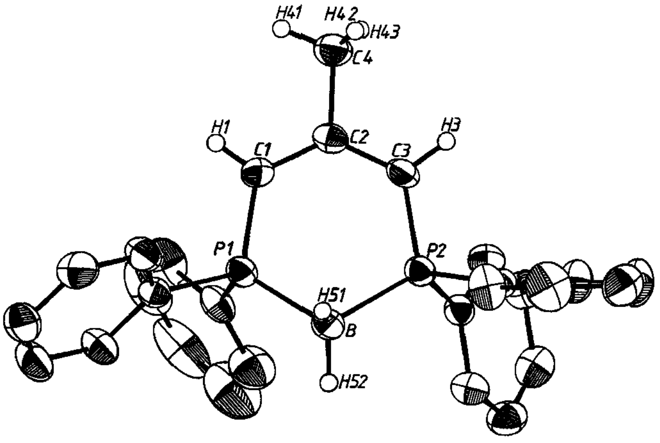


Figure 1. Molecular structure of **3** with the atom numbering scheme (ORTEP, 50% probability ellipsoids are shown for the heavier atoms, arbitrary radii are used for hydrogen atoms, phenyl-hydrogen atoms are omitted)

The molecule exhibits very short P−C bonds [P1−C1 = 1.728(2), P2−C3 = 1.736(2)Å], which indicate some ylidic character of the allylic fragment. The ring−methyl distance C3−C4 [1.508(3)Å] lies definitely in the range of

C—C single-bond lengths, while the bond lengths C1—C2 [1.397(3)Å] and C3—C2 [1.387(3)Å] are intermediate between a C—C bond and e.g. the exocyclic C=C bond found in **1**[8]. These data are in good agreement with the methallyl anion character of the corresponding structural unit and a delocalized allylic system.

Table 3. Bond distances [Å] and angles [°] in **3**

bond lengths			
*P1-C1	1.728(2)	*P2-C3	1.736(2)
*C2-C1	1.397(3)	*C2-C3	1.387(3)
*C2-C4	1.508(3)		
P1-B	1.924(2)	P2-B	1.923(3)
P1-C11	1.829(2)	P2-C21	1.816(2)
P1-C12	1.817(2)	P2-C22	1.820(2)
bond angles			
*P1-C1-C2	125.4(2)	*P2-C3-C2	123.9(2)
*C1-C2-C4	114.5(2)	*C3-C2-C4	116.5(2)
*C1-C2-C3	129.0(2)		
B-P1-C1	111.2(1)	B-P2-C3	110.5(1)
B-P1-C11	112.8(1)	B-P2-C21	109.3(1)
B-P1-C12	111.7(1)	B-P2-C22	113.3(1)
P1-B-P2	106.0(1)		
C1-P1-C11	111.6(1)	C3-P2-C21	107.8(1)
C1-P1-C12	107.0(1)	C3-P2-C22	111.4(1)
C11-P1-C12	102.0(1)	C21-P2-C22	104.2(1)

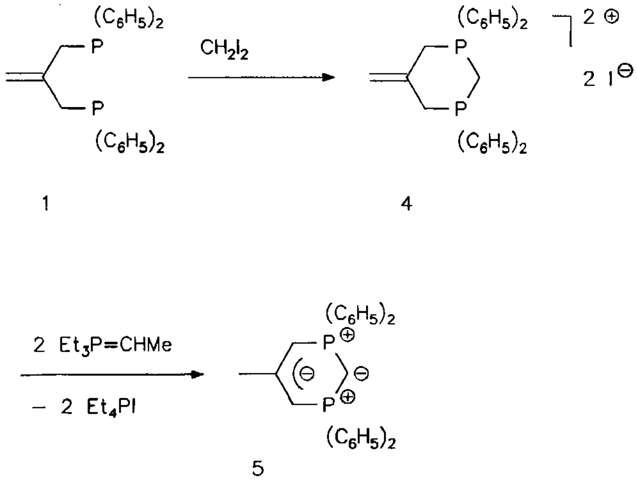
*Parameters of the methallylic fragment.

The average of the two P—B distances [1.924(3)Å] agrees with P—B distances in a variety of six-membered rings containing $R_2P-BH_2-PR_2$ moieties[11]; the folding angle of the half-chair is 144.0(2)°. All hydrogen atoms could be located and refined isotropically.

Synthesis and Molecular Structure of the 1λ⁵,3λ⁵-Diphosphabenzene 5

The diiodide **4** is readily obtained by the reaction of 1,1-bis[(diphenylphosphino)methyl]ethene (**1**) with diiodomethane[9]. Dehydrohalogenation with triethyl(ethylidene)phosphorane yields the title compound **5** in high yields (Scheme 2). The spectroscopic data provide ample support for the proposed structure.

Scheme 2



The X-ray structure analysis of **5** shows the absence of crystallographical symmetry in the crystalline state which is mainly due to the different orientations of the phenyl groups [angles between normals to planes: ring(C11) and ring(C12) = 107.66°, ring(C21) and ring(C22) = 90.04°], but the molecular geometry is still close to the expected C_{2v} (or C_s) symmetry (**Figure 2**). The ring system is almost planar (with a maximum deviation from planarity for C1 of 0.03Å). Accordingly, the sum of the internal angles at the ring atoms is 719.9°. However, the internal angles at C1, C2, and C3 are significantly larger than 120°, and those at P1 and P2 significantly smaller (Table 4). The P1—C5 and P2—C5 distances (average 1.697Å) as well as the P1—C1 and P2—C3 distances (average 1.726Å) reflect the ylidic character of **4**, as also suggested by the much longer P—C-(phenyl) distances (average 1.827Å), used as reference data. The C2—C4 distance [1.516(4)Å] is indicative of a C—C

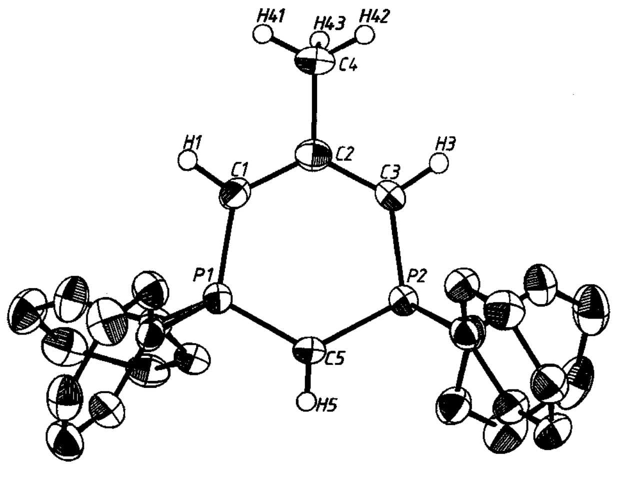


Figure 2. Molecular structure of **5** with atom numbering scheme (ORTEP see Figure 1)

Table 4. Selected interatomic distances [Å] and angles [°] in **5**

bond lengths			
*P1-C1	1.729(3)	*P2-C3	1.724(3)
*C2-C1	1.387(4)	*C2-C3	1.393(4)
*C2-C4	1.516(4)		
P1-C5	1.699(3)	P2-C5	1.695(3)
P1-C11	1.819(3)	P2-C21	1.833(3)
P1-C12	1.827(3)	P2-C22	1.828(3)
bond angles			
*P1-C1-C2	124.2(2)	*P2-C3-C2	124.2(2)
*C1-C2-C4	116.2(2)	*C3-C2-C4	116.0(2)
*C1-C2-C3	127.8(3)		
C5-P1-C1	110.2(1)	C5-P2-C3	110.4(1)
C5-P1-C11	112.8(1)	C5-P2-C21	111.6(1)
C5-P1-C12	110.0(1)	C5-P2-22	111.3(1)
P1-C5-P2	123.1(2)		
C1-P1-C11	110.0(1)	C3-P2-C21	111.5(1)
C1-P1-C12	111.2(1)	C3-P2-C22	110.4(1)
C11-P1-C12	102.4(1)	C21-P2-C22	101.3(1)

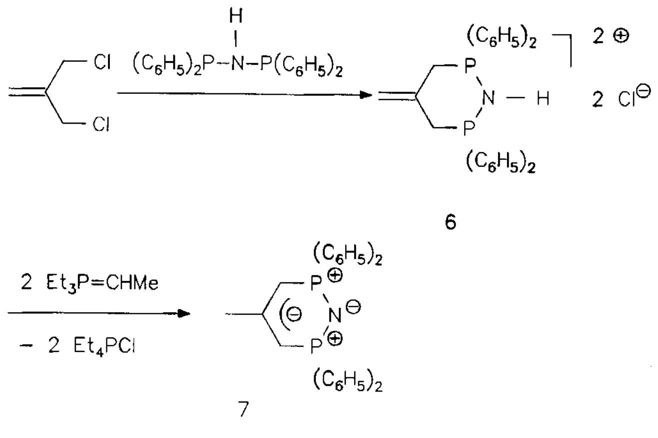
*Parameters of the methallylic fragment.

bond, as opposed to the double-bond value for the starting material **1** [1.307(5)Å][8]. Moreover, the methyl hydrogen atoms can be located in the final refinement of the structure (and confirmed by the ^{1}H-coupled ^{13}C-NMR spectra). The C1–C2 and C3–C2 distances with the average value of 1.390Å are in agreement with the methallyl anion character of the corresponding structural unit.

Preparation, Spectroscopic Data, and Crystal Structure of the 2-Aza-1λ^5,3λ^5-diphosphabenzene 7

For the preparation of the cyclic diphosphazane a strategy for the cylization like that employed for the previous compounds **2** and **4** has not been possible. Strongly oxidizing agents like [NHCl$_2$][12] are likely to destroy the cyclization reagent 1,1-bis[(diphenylphosphino)methyl]ethene. With the synthesis of 1,1,3,3-tetraphenyldiphosphazane[13] both the (Ph$_2$P–NH–PPh$_2$) subunit and an excellent substrate with two nucleophilic phosphorus atoms have been obtained. Through quaternization of this diphosphazane with 3-chloro-2-chloromethyl-1-propene a suitable precursor of the 2-aza-1,3-diphosphabenzene **7** can be prepared in good yields .

Scheme 3



The NMR spectra (Table 1), elemental analyses, and mass spectra confirm the proposed composition of **6**. In the ^{1}H-decoupled ^{31}P-NMR spectrum a single resonance is observed which is shifted to higher field. The NH proton is subject to rapid exchange in the polar solvents needed for efficient solvation of the salt.

For the creation of the methallyl moiety [CHC(Me)CH]$^\ominus$ and the deprotonation of the nitrogen atom the same reaction conditions are used as for compounds **3** and **5**. The yellow product **7** is obtained in good yield and characterized by NMR spectroscopy and mass spectrometry, elemental and X-ray structure analysis.

In a monoclinic cell (space group *P*2/*c*, no. 13) two half molecules of **7** are found in the asymmetric unit. In both fragments (A,B) the atoms N, P1, C2, and C4 lie on a twofold crystallographic axis (Table 5). The H atoms of the exocyclic methyl groups show a distinct disorder under these symmetry conditions. Since the two molecules differ only slightly in their geometrical parameters, only molecule A is shown in Figure 3. The two crystallographically independent heterocycles obey C_2 symmetry [angles between normals to planes: molecule A: ring(C11) and ring(C12) = 66.64°; molecule B: ring(C11) and ring(C12) = 90.30°]. The ring system of molecule A has an almost planar geometry (with a maximum deviation from planarity for C1 of 0.05Å), but the ring of molecule B is more strongly distorted (maximum deviation for C1 of 0.10Å). In both cases, the sum of the angles at C2 is exactly 360°, and correspondingly the sum of the internal angles at the ring atoms deviates only slightly from 720° (A: 719.4°; B: 717.2°).

Table 5. Selected interatomic distances [Å] and angles [°] in the two independent molecules A and B of 7 (for each independent molecule one half is generated through space-symmetry conditions)

	molecule A[a]	molecule B[b]
bond lengths		
*P1/P1′-C1/C1′	1.724(2)	1.723(2)
*C2-C1/C1′	1.393(2)	1.391(2)
*C2-C4	1.507(4)	1.496(5)
P1/P1′-N	1.595(1)	1.596(1)
P1/P1′-C11	1.809(2)	1.806(2)
P1/P1′-C12	1.816(2)	1.820(2)
bond angles		
*P1-C1-C2	121.7(2)	121.0(2)
*C1-C2-C1′	127.0(2)	126.9(2)
*C1-C2-C4	116.5(1)	116.6(1)
N-P1-C1	112.4(1)	112.7(1)
N-P1-C11	108.04(8)	109.15(9)
N-P1-C12	107.78(7)	108.68(8)
C1-P1-C11	109.6(1)	111.0(1)
C1-P1-C12	112.10(9)	111.0(1)
C11-P1-C12	106.68(9)	103.86(9)
P1-N-P1′	124.2(1)	122.9(2)

[a] Residue 1 from symmetry operation $-x,y,-z+0.5$ and translational operation $1-x,y,z$. – [b] Residue 2 from symmetry operation $-x,y,-z+0.5$. – *Parameters of the methallylic fragment.

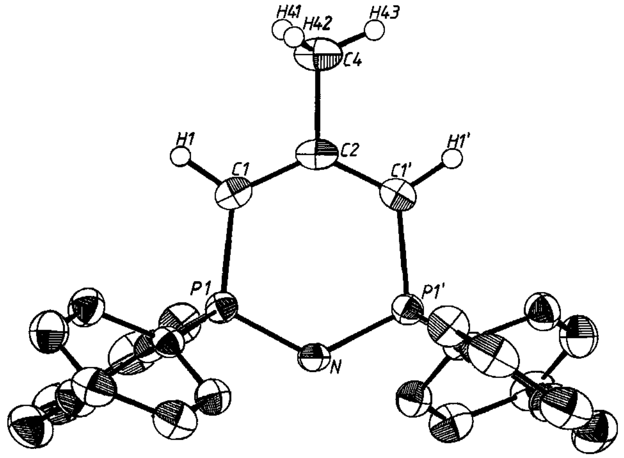


Figure 3. Molecular structure of 7 (molecule A) with atom numbering scheme and the orientation of one set of H atoms of the exocyclic methyl group (ORTEP see Figure 1)

The short distances P1–C1 [average 1.724(2) Å] are proof of the ylidic character of **7**. The C2–C4 distance [1.507(4) Å] identifies an exocyclic methyl group attached to the heterocycle by a C–C bond, and with an average value of 1.392(2) Å the distances C1–C2 indicate the allyl anion character of the corresponding structural unit.

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Experimental

General: All experiments were carried out under pure nitrogen. Glassware and solvents were purified, dried, and kept under nitrogen accordingly. For NMR spectroscopy phosphoric acid, trimethyl borate, and deuterated solvents were used as reference compounds (Jeol GX400 spectrometer).

5-Methylene-1,1,3,3-tetraphenyl-1,3-diphosphonia-2-boratacyclohexane Bromide (**2**): A solution of **1** (2.00 g, 4.71 mmol) in 50 ml of toluene was treated at −30°C with Me_2S-BH_2Br (0.73 g, 4.71 mmol). The mixture was stirred at room temp. for 18 h. The precipitate was separated and washed with 100 ml of toluene/acetone (3:1); yield 1.20 g (50%) of white powder, m.p. 215°C. – ^1H, ^{11}B, ^{13}C, ^{31}P NMR: Table 1.

$C_{28}H_{28}BBrP_2$ (517.2)	Calcd.	C 65.03 H 5.46 P 11.98
	Found	C 64.60 H 5.56 P 11.36

5-Methyl-1,1,3,3-tetraphenyl-$1\lambda^5$-phospha-3-phosphonia-2-boratabenzene (**3**): A suspension of **2** (1.20 g, 2.32 mmol) in 100 ml of THF at −78°C was treated with a solution of $Et_3P=CHMe$ (0.33 g, 2.32 mmol) in 25 ml of THF. After warming to 20°C, the reaction mixture was stirred for another 30 min. The precipitate was separated (0.25 g of Et_4PBr) and the filtrate evaporated to dryness. The product was recrystallized from Et_2O and CH_3CN; yield 0.91 g (90%) of yellow crystals, m.p. 116°C (dec.). – ^1H, ^{11}B, ^{13}C, ^{31}P NMR: Table 2. – MS (EI, 70 eV): m/z (%) = 436.2 (100) [M^+].

$C_{28}H_{27}BP_2$ (436.28)	Calcd.	C 77.08 H 6.24 P 14.20
	Found	C 75.41 H 6.44 P 14.03

Table 6. Crystal structure data for **3**, **5**, **7**

	3	**5**	**7**
Formula	$C_{28}H_{27}BP_2$	$C_{29}H_{26}P_2$	$C_{28}H_{25}NP_2$
M_r	436.28	436.48	437.46
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$ (IT. #14)	$P\bar{1}$ (IT. #2)	P2/c (IT. #13)
a [Å]	8.825(1)	3.557(1)	17.453(3)
b [Å]	16.036(2)	11.354(2)	7.995(1)
c [Å]	16.904(2)	15.306(2)	16.646(3)
α [deg]	90	113.83(1)	90
β [deg]	99.54(1)	94.96(1)	93.66(1)
γ [deg]	90	96.39(1)	90
V [Å]^3	2359.1	1181.3	2318.0
Z	4	2	4
d_{calc} [gcm^{-1}]	1.23	1.22	1.25
μ(Mo-K_α) [Å]	1.57	1.57	1.94
F(000) [e]	920	460	950
T [°C]	-50	-50	-50
Diffractometer	Syntex $P2_1$	Syntex $P2_1$	Syntex $P2_1$
Scan	ω	ω	ω
Scan width (in ω)	0.8	0.8	0.8
$(\sin \theta/\lambda)_{max}$ [Å]$^{-1}$	0.572	0.583	0.595
hkl range	±10,18,19	8,±13,±17	±20,9,19
$Refl._{measd\ unique}$	4111/3696	3909/3909	4543/4089
R_{int}	0.0243	0.0000	0.0167
$Refl._{observed}$	3078	3211	3256
Structure solution	direct methods	direct methods	direct methods
H atoms (found/calculated)	all/0	25/1	all/0
Parameters refined	388	295	394
R^a	0.0371	0.0455	0.0432
$R_w{}^b$	0.0349	0.0402	0.0354
$\Delta\rho_{fin}$(max/min) [e/Å^3]	0.264/-0.194	0.334/-0.318	0.356/-0.320

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. – [b] $R_w = [\Sigma_w(|F_o|-|F_c|)^2/\Sigma_w F_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$; function minimized: $\Sigma_w(|F_o|-|F_c|)^2$.

Table 7. Fractional atomic coordinates and equivalent isotropic displacement parameters of **3** [U(eq.) = $(U_1U_2U_3)^{1/3}$, where U_i are the eigenvalues of the U_{ij} matrix]

ATOM	X/A	Y/B	Z/C	U(eq.)
P1	0.18186(6)	0.15914(3)	0.70962(3)	0.055
P2	0.47159(6)	0.04960(3)	0.73342(3)	0.057
B	0.3820(3)	0.1468(2)	0.7739(2)	0.063
C1	0.1003(3)	0.0632(1)	0.6825(1)	0.066
C2	0.1784(2)	-0.0129(1)	0.6882(1)	0.047
C3	0.3345(3)	-0.0281(1)	0.7101(1)	0.074
C4	0.0772(3)	-0.0879(2)	0.6665(2)	0.076
C111	0.1832(2)	0.2263(1)	0.6223(1)	0.061
C112	0.2575(3)	0.3025(1)	0.6297(1)	0.066
C113	0.2455(3)	0.3564(2)	0.5647(2)	0.085
C114	0.1584(3)	0.3347(2)	0.4926(2)	0.078
C115	0.0840(3)	0.2589(2)	0.4843(1)	0.069
C116	0.0973(3)	0.2040(1)	0.5488(1)	0.063
C121	0.0504(2)	0.2141(1)	0.7635(1)	0.061
C122	-0.0677(3)	0.2626(2)	0.7231(2)	0.094
C123	-0.1773(3)	0.2971(2)	0.7625(2)	0.128
C124	-0.1706(3)	0.2842(2)	0.8433(2)	0.113
C125	-0.0539(4)	0.2369(2)	0.8846(2)	0.099
C126	0.0566(3)	0.2025(2)	0.8457(2)	0.093
C221	0.5691(3)	0.0718(2)	0.6490(1)	0.067
C222	0.5945(3)	0.1522(2)	0.6257(2)	0.108
C223	0.6678(4)	0.1663(4)	0.5598(2)	0.138
C224	0.7120(4)	0.1015(4)	0.5174(2)	0.110
C225	0.6886(4)	0.0225(4)	0.5397(2)	0.120
C226	0.6162(3)	0.0059(2)	0.6056(2)	0.093
C211	0.6221(2)	0.0092(1)	0.8103(1)	0.060
C212	0.7762(3)	0.0254(2)	0.8101(2)	0.074
C213	0.8871(3)	-0.0067(2)	0.8696(2)	0.098
C214	0.8458(3)	-0.0538(2)	0.9305(2)	0.095
C215	0.6930(3)	-0.0686(2)	0.9328(2)	0.081
C216	0.5812(3)	-0.0376(2)	0.8728(1)	0.076

Table 8. Fractional atomic coordinates and equivalent isotropic displacement parameters of **5** [U(eq.) see Table 7]

ATOM	X/A	Y/B	Z/C	U(eq.)
P1	0.29911(9)	0.59806(7)	0.35364(5)	0.054
P2	0.23502(9)	0.33485(7)	0.18879(5)	0.055
C1	0.1066(4)	0.6145(3)	0.2927(2)	0.071
C2	0.0084(3)	0.5160(3)	0.2095(2)	0.063
C3	0.0486(4)	0.3920(3)	0.1574(2)	0.060
C4	-0.1638(4)	0.5465(3)	0.1708(2)	0.102
C5	0.3581(4)	0.4495(3)	0.2921(2)	0.074
C10	0.2666(3)	0.6278(3)	0.4767(2)	0.062
C11	0.2389(4)	0.5247(3)	0.5029(2)	0.069
C12	0.1970(4)	0.5437(3)	0.5937(2)	0.079
C13	0.1828(4)	0.6685(3)	0.6598(2)	0.082
C14	0.2098(5)	0.7714(3)	0.6342(2)	0.105
C15	0.2519(4)	0.7533(3)	0.5443(2)	0.088
C20	0.4851(4)	0.7269(2)	0.3718(2)	0.060
C21	0.6320(4)	0.7587(3)	0.4429(2)	0.072
C22	0.7821(4)	0.8451(3)	0.4475(2)	0.097
C23	0.7854(4)	0.9009(3)	0.3830(2)	0.089
C24	0.6383(4)	0.8714(3)	0.3125(2)	0.086
C25	0.4890(4)	0.7834(3)	0.3066(2)	0.074
C30	0.1720(4)	0.1804(3)	0.1984(2)	0.062
C31	0.0330(4)	0.0862(3)	0.1326(2)	0.082
C32	-0.0160(5)	-0.0305(3)	0.1402(3)	0.104
C33	0.0744(5)	-0.0557(3)	0.2114(3)	0.117
C34	0.2127(5)	0.0362(3)	0.2761(2)	0.109
C35	0.2603(4)	0.1546(3)	0.2702(2)	0.085
C40	0.3699(3)	0.2850(2)	0.0902(2)	0.054
C41	0.4841(4)	0.1928(3)	0.0785(2)	0.085
C42	0.5913(4)	0.1631(3)	0.0050(2)	0.103
C43	0.5854(4)	0.2237(3)	-0.0567(2)	0.082
C44	0.4712(4)	0.3156(3)	-0.0456(2)	0.078
C45	0.3647(4)	0.3456(3)	0.0270(2)	0.074

5-Methylene-1,1,3,3-tetraphenyl-1,3-diphosponiacyclohexane Diiodide (**4**): A solution of **1** (2.00 g, 4.71 mmol) in 50 ml of dichloromethane was treated at room temp. with diiodomethane (1.26 g, 0.38 ml, 4.71 mmol) and stirred at 35°C for 2 d. The precipitate was separated, washed with pentane, and dried in vacuo; yield 1.50 g (46%) of white powder, m.p. 215°C (dec.). – ^{1}H, ^{13}C, ^{31}P NMR: Table 1.

$C_{29}H_{28}I_2P_2$ (692.28) Calcd. C 50.31 H 4.08
Found C 50.65 H 4.19

5-Methyl-1,1,3,3-tetraphenyl-$1\lambda^5,3\lambda^5$-diphosphabenzene (**5**): A suspension of **4** (0.58 g, 0.84 mmol) in 50 ml of THF at −78°C was treated with a solution of $Et_3P=CHMe$ (0.25 g, 1.68 mmol) in 25 ml of THF. After warming to 20°C, the reaction mixture was stirred for another 10 min. The precipitate was separated (0.40 g of Et_4PI) and the filtrate evaporated to dryness in vacuo and cooled until crystallization of **5** started (at −25°C); yield 0.32 g (87%) of yellow crystals, m.p. 115°C (dec.). – ^{1}H, ^{13}C, ^{31}P NMR: Table 2.

$C_{29}H_{26}P_2$ (436.46) Calcd. C 79.80 H 6.00 P 14.19
Found C 78.27 H 6.29 P 14.05

5-Methylene-1,1,3,3-tetraphenyl-2-aza-1,3-diphosphoniacyclohexane Dichloride (**6**): A suspension of 1,1,3,3-tetraphenyldiphosphazane (6.90 g, 17.9 mmol) in 50 ml of toluene at 20°C was treated with a solution of 3-chloro-2-chloromethyl-1-propene (2.24 g, 17.9 mmol) in 20 ml of toluene. The reaction mixture was stirred at 40°C for 5 d, the product separated and washed with benzene; yield 4.00 g (43%) of white solid, m.p. 218°C (dec.). – ^{1}H, ^{13}C, ^{31}P NMR: Table 1. – MS(FD): *m/z* (%) = 438.1 (100) $[M-H^+, 2\ Cl^-]$.

$C_{28}H_{27}Cl_2NP_2$ (510.39)
Calcd. C 65.89 H 5.33 Cl 13.90 N 2.74 P 12.14
Found C 66.07 H 5.74 Cl 11.08 N 3.97 P 12.08

Table 9. Fractional atomic coordinates and equivalent isotropic displacement parameters of **7** [*U*(eq.) see Table 7].

ATOM	X/A	Y/B	Z/C	U(eq.)
N1	0.50000	0.2230(3)	0.25000	0.024
P1	0.48755(3)	0.12965(6)	0.33281(3)	0.022
C11	0.4940(1)	-0.0847(3)	0.3242(1)	0.028
C12	0.50000	-0.1624(3)	0.25000	0.027
C13	0.50000	-0.3509(4)	0.25000	0.037
C111	0.5598(1)	0.2039(3)	0.4071(1)	0.024
C112	0.6354(1)	0.1608(3)	0.3931(1)	0.036
C113	0.6957(1)	0.2171(3)	0.4435(2)	0.042
C114	0.6817(2)	0.3160(3)	0.5084(2)	0.040
C115	0.6081(2)	0.3600(3)	0.5233(2)	0.044
C116	0.5465(1)	0.3053(3)	0.4724(1)	0.037
C121	0.3953(1)	0.1951(2)	0.3666(1)	0.022
C122	0.3674(1)	0.1316(3)	0.4372(1)	0.034
C123	0.2952(1)	0.1781(3)	0.4595(1)	0.039
C124	0.2502(1)	0.2839(3)	0.4110(1)	0.036
C125	0.2765(1)	0.3455(3)	0.3410(1)	0.038
C126	0.3491(1)	0.3014(3)	0.3183(1)	0.028
N2	0.00000	0.7917(3)	0.25000	0.024
P2	0.07386(3)	0.88708(6)	0.28848(3)	0.021
C21	0.0690(1)	1.1003(3)	0.2740(1)	0.026
C22	0.00000	1.1781(3)	0.25000	0.030
C23	0.00000	1.3652(5)	0.25000	0.049
C211	0.1588(1)	0.8009(3)	0.2477(1)	0.024
C212	0.2317(1)	0.8468(3)	0.2796(1)	0.033
C213	0.2962(1)	0.7892(3)	0.2447(2)	0.039
C214	0.2895(1)	0.6847(3)	0.1792(1)	0.047
C215	0.2182(1)	0.6371(3)	0.1476(1)	0.045
C216	0.1526(1)	0.6953(3)	0.1816(1)	0.031
C221	0.0853(1)	0.8361(3)	0.3952(1)	0.028
C222	0.0852(2)	0.6700(3)	0.4195(1)	0.040
C223	0.0891(2)	0.6291(4)	0.5004(2)	0.048
C224	0.0944(1)	0.7533(5)	0.5575(2)	0.062
C225	0.0955(2)	0.9160(5)	0.5344(2)	0.068
C226	0.0910(1)	0.9589(4)	0.4532(1)	0.048

5-Methyl-1,1,3,3-tetraphenyl-2-aza-$1\lambda^5,3\lambda^5$-diphosphabenzene (**7**): A suspension of **6** (1.00 g, 2.00 mmol) in 100 ml of THF was treated at −78°C with a solution of $Et_3P=CHMe$ (0.58 g, 4.00 mmol) in 25 ml of THF. After warming to 20°C, the reaction mixture was stirred for another 30 min. The precipitate was separated (0.66 g of Et_4PCl) and the filtrate evaporated to dryness. The product was recrystallized from Et_2O and CH_3CN; yield 0.52 g (60%) of yellow crystals, m.p. 118°C. – ^{1}H, ^{13}C, ^{31}P NMR: Table 2. – MS (EI, 70 eV): *m/z* (%) = 437 (100) $[M^+]$.

$C_{28}H_{25}NP_2$ (437.46) Calcd. C 76.87 H 5.76 N 3.20 P 14.16
Found C 76.91 H 5.89 N 3.13 P 14.54

X-ray Structure Analyses of Compounds **3**, **5**, **7**[14]: Suitable single crystals of **3**, **5**, **7** were mounted in glass capillaries under argon and examined directly on the diffractometer. Crystal data and important numbers pertinent to data collection and refinement are collected in Table 6. The data sets were recorded with Mo-K_α radiation (λ = 0.71069 Å) by using a graphite monochromator. They were corrected for Lp effects and empirically for those of absorption. Structure factors with $F_o \geq 4\sigma(F_o)$ were considered "observed" and used for refinement. Tables 7, 8, 9 contain the atomic coordinates of the non-hydrogen atoms. – Programs used were DELOS, LEPAGE (cell reduction), SHELXS-86 (structure solution), SHELX-76 (structure refinement), and local routines.

CAS Registry Numbers

1: 120658-80-2 / **2**: 120883-38-7 / **3**: 132749-41-8 / **4**: 123775-77-9 / **5**: 125995-74-6 / **6** (phosphorane): 132724-12-0 / **6** (phosphonium): 132724-14-2 / **7**: 132724-13-1 / Me_2S-BH_2Br: 55652-52-3 / $Et_3P=CHCH_3$: 17847-85-7 / CH_2I_2: 75-11-6 / $(C_6H_5)_2PNHP(C_6H_5)_2$: 2960-37-4 / $H_2C=C(CH_2Cl)_2$: 1871-57-4

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[14] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository numbers CSD-54502/55204, the names of the authors, and the journal citation.

[25/91]