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# More user-friendly phosphines? Molecular structure of methylphosphine and its adduct with borane, studied by gas-phase electron diffraction and quantum chemical calculations†

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The molecular structures of methylphosphine ( $\text{CH}_3\text{PH}_2$ ) and methylphosphine–borane ( $\text{CH}_3\text{PH}_2\cdot\text{BH}_3$ ) have been determined from gas-phase electron diffraction data and rotational constants, employing the SARACEN method. The experimental geometric parameters generally showed a good agreement with those obtained using *ab initio* calculations and previous microwave spectroscopy studies. In order to assess the accuracy of the calculated structures a range of *ab initio* methods were used, including the CCSD(T) method, with correlation-consistent basis sets. The structural environment around the phosphorus atom was found to change significantly upon complexation with borane, with the P–C bond length shortening and the bond angles widening.

## Introduction

Relatively few studies have been conducted on the structures of the primary aliphatic phosphines,  $\text{R–PH}_2$ , and they are less widely used throughout chemistry than the aryl phosphines. This is due to their unfavourable properties; they are often pyrophoric, toxic, unstable in air and possess unpleasant odours. Primary phosphines have potential as starting materials for various applications<sup>1</sup> and therefore the development of more air-stable, *user-friendly* phosphines is of great interest. Increased air and moisture stability can be achieved by the addition of a bulky protecting group, for example the mesityl group in mesitylphosphine,<sup>2</sup> or by complexation with a suitable Lewis acid. Complexes with borane have been reported and the chemistry of the adducts explored<sup>3</sup> but only a few structural studies have been reported.<sup>4</sup> Tertiary phosphine–borane complexes are considered to be protected free phosphines, with the free phosphine easily recovered by reaction with excess amine. It has been shown that the same is possible for primary phosphines, albeit with a reduced yield.<sup>3</sup> The gas phase electron diffraction (GED) study of methylphosphine (**1**) and methylphosphine–borane (**2**), as one of the simplest examples of a primary phosphine and its borane adduct, provides a starting point for the investigation of larger functionalised primary phosphines. The degree of increased stability imparted by formation of the adduct is of particular interest, especially with regard to the structural changes accompanying the complexation. Studying a simple system such as methylphosphine allows analysis of these phenomena without the increased complexity that would

be present in larger molecules. **1** and **2** also present the opportunity to conduct high-level *ab initio* calculations, which would be prohibitively expensive for much larger phosphines. The GED study of larger phosphines will rely more heavily on the use of *ab initio* data via the SARACEN method,<sup>5–7</sup> and so it is vital to gauge the accuracy of various theoretical methods in order to identify suitable computational techniques for future work.

Lewis acid–base adducts are also interesting in a more general sense. Previous research has found large deviations between the gas phase and crystalline structures of some Lewis acid–base adducts; for example, in  $\text{HCN–BF}_3$  the B–N bond length is found to be 83.5(31) pm shorter in the crystalline solid than in the gas phase.<sup>8</sup> It is therefore apparent that the bond between such a Lewis acid–base complex can be significantly shortened by the effects of crystal packing<sup>9</sup> and so it is vital that the structure is studied in the gas phase, free from the potential distortions present in the crystalline solid.

The structures of both systems have previously been studied to some degree, with a structure of **2**, determined by microwave (MW) spectroscopy, yielding a P–B bond length of 190.6(6) pm,<sup>10</sup> close to the sum of the covalent radii for the two atoms. **1** has previously been studied by both GED<sup>11</sup> and MW spectroscopy,<sup>12</sup> but both studies failed to yield complete structures. We have revisited both compounds utilising modern GED techniques and analysis methods to allow complete structural determination for both molecules using a combination of GED data and published rotational constants. Such an analysis allows us to draw conclusions on the effects of complexation using comparable results.

## Experimental

### Synthesis

The syntheses of methylphosphine,<sup>3,13</sup> diborane<sup>14</sup> and methylphosphine–borane<sup>3,15</sup> are given in the ESI.†

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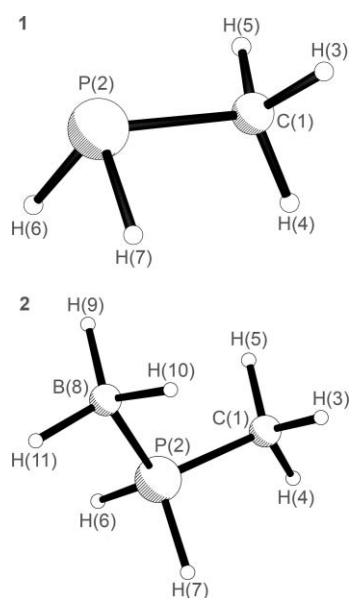
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† Electronic supplementary information (ESI) available: Syntheses, GED parameters, molecular geometries, interatomic distances, amplitudes of vibration, least-squares correlation matrices, experimental gas-phase electron diffraction coordinates and experimental–theoretical molecular scattering intensities for (**1**) and (**2**). For ESI see DOI: 10.1039/b804780d

## Theoretical methods

Calculations for methylphosphine were performed using a Linux cluster, whilst those for methylphosphine–borane were performed using a Silicon Graphics Altix 4700, both using the Gaussian 03 program.<sup>16</sup> All MP2 methods were frozen core (fc).

**Geometry optimisations.** An extensive search of the torsional potential of each compound was undertaken at the RHF/3–21G\* level<sup>17–19</sup> to locate all minima. For each molecule one minimum with  $C_s$  symmetry was located. Further geometry optimisations were conducted for both molecules at the HF,<sup>20</sup> MP2<sup>21</sup> and CCSD(T)<sup>22–25</sup> levels of theory. At the MP2 and CCSD(T) levels optimisations were conducted using both the Pople-type basis sets (6–31G\*<sup>26–28</sup> and 6–311G\*<sup>29,30</sup>) and the correlation-consistent basis sets of Dunning and co-workers.<sup>31–35</sup> The optimised structures of **1** and **2** with the atomic numbering schemes are shown in Fig. 1.



**Fig. 1** Molecular structures of methylphosphine (**1**) and methylphosphine–borane (**2**).

**Frequency calculations.** Analytic second derivatives<sup>36,37</sup> of the energies with respect to nuclear coordinates calculated at the MP2/

6–311++G\*\* level for **1** and **2** served both to confirm the nature of the minima found by the optimisation and to provide vibrational information for use in the SARACEN refinement.

## Gas electron diffraction measurements

Data were collected for methylphosphine and methylphosphine–borane using the Edinburgh gas-diffraction apparatus.<sup>38</sup> For each molecule, an accelerating voltage of *ca.* 40 kV (electron wavelength *ca.* 6.0 pm) was used. Sample and nozzle temperatures were maintained at 220 and 293 K, respectively, for **1** and 300 and 320 K, respectively, for **2**. Scattering intensities were recorded on Kodak electron image films at nozzle-to-plate distances of 127.8 and 284.6 mm for **1** and 92.0 and 249.2 mm for **2**. The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for the two camera distances for each molecule are given in Table S1† in the ESI, together with electron wavelengths, which were determined from the scattering patterns of benzene vapour, recorded immediately after the compound patterns and analysed in exactly the same way to minimise systematic errors in wavelengths and camera distances. The scattering intensities were measured using an Epson Expression 1680 Pro flatbed scanner and converted to optical densities as a function of the scattering variable, *s*, using an established program.<sup>39</sup> Data reduction and least-squares refinements were carried out using the ed@ed v2.4 program,<sup>40</sup> employing the scattering factors of Ross *et al.*<sup>41</sup>

## Results

### Ab initio calculations

**Methylphosphine.** The lowest-energy structure of methylphosphine on the potential-energy surface had a staggered conformation and possessed  $C_s$  symmetry. The effects of improving the basis set and description of electron correlation on the structural parameters were gauged by a series of calculations at the MP2 and CCSD(T) levels of theory using both Pople-type and correlation-consistent basis sets. The results of selected calculations are shown in Table 1 with the full results from geometry optimisations given in the ESI, in Table S2 and Table S3.†

The structure of **1** was found to be largely independent of the level of theory used, with two main exceptions. In the

**Table 1** Molecular geometries of the lowest-energy structures of methylphosphine (**1**) at the MP2 and CCSD(T) levels of theory<sup>a</sup>

	MP2		CCSD(T)	
	6–311++G**	aug-cc-pVQZ	6–311++G**	aug-cc-pVQZ <sup>b</sup>
$r_{C(1)-H(3)}/\text{pm}$	109.2	108.7	109.6	109.1
$r_{C(1)-H(4)}/\text{pm}$	109.1	108.5	109.4	108.9
$r_{C(1)-P(2)}/\text{pm}$	185.6	185.1	186.7	185.9
$r_{P(2)-H(6)}/\text{pm}$	141.0	141.1	141.7	141.7
$\angle P(2)-C(1)-H(3)/^\circ$	109.0	108.6	109.0	108.9
$\angle P(2)-C(1)-H(4)/^\circ$	113.8	113.4	113.6	113.2
$\angle H(3)-C(1)-H(4)/^\circ$	108.7	109.2	108.7	109.2
$\angle H(3)-C(1)-H(5)/^\circ$	107.5	107.7	107.6	107.8
$\angle C(1)-P(2)-H(6)/^\circ$	97.6	97.8	97.2	97.6
$\angle H(6)-P(2)-H(7)/^\circ$	94.6	93.5	94.4	93.3
Energy/Hartrees	-381.8117	-381.9166	-381.8599	-381.9685

<sup>a</sup> See Fig. 1 for atom numbering. <sup>b</sup> Extrapolated using  $\text{CCSD(T)/aug-cc-pVQZ} = \text{CCSD(T)/aug-cc-pVTZ} + [\text{MP2/aug-cc-pVQZ} - \text{MP2/aug-cc-pVTZ}]$ .

**Table 2** Molecular geometries of the lowest-energy structure of methylphosphine–borane (**2**) at the MP2 and CCSD(T) levels of theory<sup>a</sup>

Parameter	MP2		CCSD(T)	
	6-311++G**	aug-cc-pVQZ	6-311++G**	aug-cc-pVQZ <sup>b</sup>
<i>r</i> C(1)–H(3)/pm	109.2	108.7	109.5	109.0
<i>r</i> C(1)–H(4)/pm	109.1	108.5	109.4	108.9
<i>r</i> C(1)–P(2)/pm	182.1	181.3	182.9	182.2
<i>r</i> P(2)–H(6)/pm	140.1	140.0	140.5	140.5
<i>r</i> P(2)–B(8)/pm	192.8	191.4	193.9	192.5
<i>r</i> B(8)–H(9)/pm	120.9	120.6	121.3	121.1
<i>r</i> B(8)–H(11)/pm	120.6	120.2	121.0	120.6
∠P(2)–C(1)–H(3)/°	108.6	108.1	108.6	108.3
∠P(2)–C(1)–H(4)/°	112.3	112.4	112.2	112.0
∠H(3)–C(1)–H(4)/°	109.5	109.9	109.5	109.9
∠H(3)–C(1)–H(5)/°	108.2	108.3	108.4	108.4
∠C(1)–P(2)–H(6)/°	103.2	103.5	103.1	103.4
∠H(6)–P(2)–H(7)/°	100.3	99.8	100.3	99.7
∠C(1)–P(2)–B(8)/°	115.0	114.5	115.2	114.7
∠P(2)–B(8)–H(9)/°	103.3	102.8	103.4	102.9
∠P(2)–B(8)–H(11)/°	106.1	106.3	106.0	106.4
∠H(9)–B(8)–H(10)/°	113.7	113.8	113.8	113.7
∠H(9)–B(8)–H(11)/°	114.3	114.7	114.3	114.7
Energy/Hartrees	–408.3568	–408.4922	–408.4268	–408.5644

<sup>a</sup> See Fig. 1 for atom numbering. <sup>b</sup> Extrapolated using CCSD(T)/aug-cc-pVQZ = CCSD(T)/aug-cc-pVTZ + [MP2/aug-cc-pVQZ–MP2/aug-cc-pVTZ].

MP2 optimisations using Pople-type basis sets the P–H distance shortens by 0.7 pm when polarisation functions are added to the H atoms, indicating the need for such functions to describe this bond accurately. The C–P bond length is also sensitive to the level of theory, varying by 1.6 pm in the calculations shown in Table 1.

**Methylphosphine–borane.** The lowest-energy structure of methylphosphine–borane on the potential energy surface was an all-staggered conformation with *C<sub>s</sub>* symmetry, and the same series of calculations was performed as for **1**.

A selection of the structural parameters and energies from these calculations is given in Table 2 with the full results from the series of optimisations given in Table S4 and Table S5 in the ESI.† The absolute values of most of the structural parameters were found to be independent of the level of theory and basis set used. However, the C–P and P–B bond lengths were found to vary significantly across the range of calculations performed. In calculations with the largest basis sets the C–P bond length varied from 181.3 pm to 182.9 pm and the P–B bond varied from 191.4 pm to 193.9 pm. In both cases the CCSD(T) calculations produced longer bond lengths than MP2, and the Pople-type basis sets produced longer bond lengths than the correlation-consistent basis sets.

### Gas phase electron diffraction refinements

**Methylphosphine.** On the basis of the *ab initio* calculations described above, electron-diffraction refinements were carried out using a model with appropriate *C<sub>s</sub>* symmetry. The calculations show that the CH<sub>3</sub> group does not possess local *C<sub>3</sub>* symmetry, with the C–H(3) and C–H(4) bond lengths differing by only 0.2 pm and the H(3)–C–H(4) and H(3)–C–H(5) angles by ~1°. The difference in the C–H bond lengths of 0.2 pm is too small to be differentiated by the diffraction experiment, so the C–H bond lengths in the CH<sub>3</sub> group were modelled by a single parameter. The deviation in the angle is more pronounced and was therefore included in the model.

The structure of **1** was defined in terms of eight independent geometric parameters, comprising three bond lengths and five bond angles (Table 3, atom numbering shown in Fig. 1). The C, P and H(4) atoms lie on the mirror plane of the molecule. The C–H bond lengths were modelled by a single parameter (*p*<sub>1</sub>) and the P–C (*p*<sub>2</sub>) and P–H (*p*<sub>3</sub>) bond lengths were also included. The two P–C–H angles were defined by the average (*p*<sub>4</sub>) and difference (*p*<sub>5</sub>), given

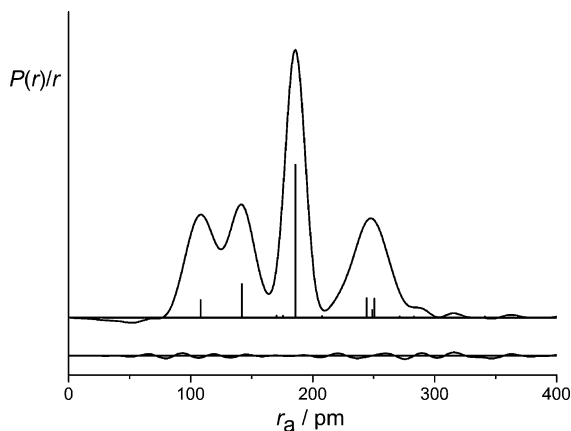
**Table 3** Refined and calculated geometric parameters for methylphosphine (**1**) from the GED study and rotational constants, in MHz, used in the GED refinements<sup>a,b</sup>

Parameter	MP2/ 6-311++G**	SARACEN ( <i>r</i> <sub>hi</sub> )	Restraint	
Independent parameters				
<i>p</i> <sub>1</sub>	<i>r</i> C(1)–H(3)/pm	109.2	108.0(1)	109.1(10)
<i>p</i> <sub>2</sub>	<i>r</i> C(1)–P(2)/pm	185.6	185.72(6)	—
<i>p</i> <sub>3</sub>	<i>r</i> P(2)–H(6)/pm	141.0	142.1(1)	—
<i>p</i> <sub>4</sub>	∠P(2)–C(1)–H <sub>av.</sub> /°	111.4	111.7(4)	—
<i>p</i> <sub>5</sub>	∠P(2)–C(1)–H <sub>diff.</sub> /°	2.4	2.4(4)	2.4(4)
<i>p</i> <sub>6</sub>	∠H(3)–C(1)–H(4)/°	108.7	109.0(9)	—
<i>p</i> <sub>7</sub>	∠C(1)–P(2)–H(6)/°	97.6	97.4(8)	97.6(10)
<i>p</i> <sub>8</sub>	∠H(6)–P(2)–H(7)/°	94.6	94.2(8)	94.6(10)
Dependent parameters				
<i>dp</i> <sub>1</sub>	∠P(2)–C(1)–H(3)/°	109.0	109.4(4)	—
<i>dp</i> <sub>2</sub>	∠P(2)–C(1)–H(4)/°	113.8	114.1(6)	—
Rotational constants				
Constant	Experimental	GED	Exp.–GED	Uncertainty
<i>B<sub>z</sub></i>	11795.10	11795.08	0.02	0.25
<i>B<sub>z</sub>–A<sub>z</sub></i>	–61129.20	–61082.05	–47.15	114.00
<i>B<sub>z</sub>–C<sub>z</sub></i>	113.00	113.01	–0.01	0.20

<sup>a</sup> Figures in parentheses are the estimated standard deviation of the last digits. <sup>b</sup> See text for parameter definitions.

by  $[P(2)-C(1)-H(4) + P(2)-C(1)-H(3)]/2$  and  $[P(2)-C(1)-H(4)-P(2)-C(1)-H(3)]/2$ , respectively. The remaining bond angles were  $\angle H(3)-C(1)-H(5)$  ( $p_6$ ),  $\angle C(1)-P(2)-H(6)$  ( $p_7$ ) and  $H(6)-P(2)-H(7)$  ( $p_8$ ). To allow for deviations from perfect  $C_s$  symmetry the  $H(3)-C(1)-P(2)-X$  dihedral angle was included as a parameter, where X is defined as the  $H(6)-P(2)-H(7)$  bisector. However, no significant deviations were found from the  $C_s$  symmetry and so this parameter was not included in the final refinement.

The starting parameters for the  $r_{hi}$  refinement<sup>42</sup> were taken from the theoretical geometry optimised at the MP2/6-311++G\*\* level. A theoretical Cartesian force field was obtained at this level and converted into a force field described by a set of symmetry coordinates using the SHRINK program,<sup>42</sup> which generated both the amplitudes of vibration ( $u_{hi}$ ) and the curvilinear corrections ( $k_{hi}$ ). All eight geometric parameters and four groups of vibrational amplitudes were then refined. Flexible restraints were employed during the refinement using the SARACEN method.<sup>5-7</sup> Altogether, four geometric restraints (Table 3) and one amplitude restraint (Table S6)† were employed. The success of the final refinement, for which  $R_G = 0.081$  ( $R_D = 0.055$ ), can be assessed on the basis of the radial distribution curve (Fig. 2) and the molecular scattering intensity curves (Fig. S1).† The final refined parameters are listed in Table 3. The ESI contains the interatomic distances and the corresponding amplitudes of vibration (Table S6), with the least-squares correlation matrix (Table S7) and the experimental coordinates from the GED analysis (Table S8).†

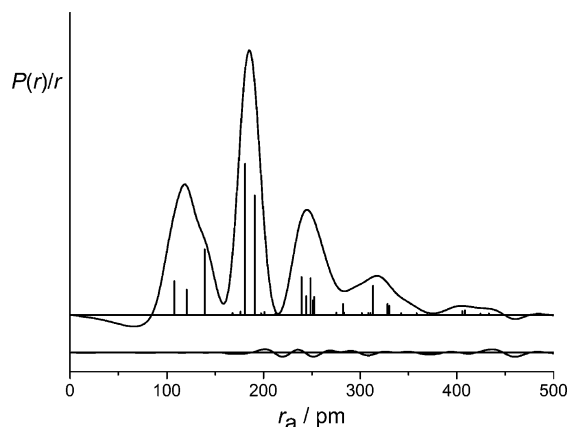


**Fig. 2** Experimental and difference (experimental–theoretical) radial distribution curves,  $P(r)/r$ , for methylphosphine (**1**). Before Fourier inversion the data were multiplied by  $s \times \exp(-0.00002s^2)/(Z_C - f_C)(Z_P - f_P)$ .

Three rotational constants for **1** were combined with the GED data.<sup>12</sup> The rotational constants  $A_0$ ,  $B_0$  and  $C_0$  were corrected to  $A_z$ ,  $B_z$  and  $C_z$  for the structural refinements using values calculated by SHRINK,<sup>42</sup> based on the MP2/6-311++G\*\* force field. The three corrected rotational constants were included in the refinements as the absolute value of  $B_z$ , and the differences  $B_z - A_z$  and  $B_z - C_z$ . These constants are given in Table 3. The vibrational corrections to the rotational constants, which transform, for example,  $A_0$  into  $A_z$ , are summations of the corrections for each of the normal modes of **1**. For the rotational constant  $A$  this correction was 1141.3 MHz and for  $B$  and  $C$  it was 2.5 and 4.4 MHz, respectively. The uncertainties of the vibrational corrections to the rotational constants were taken as 10% of the value of the vibrational

correction for  $B$  and 10% of the difference between the corrections for the two differences. The 10% figure is standard for vibrational corrections to rotational constants, based on our experience of how these quantities vary with the computational method used. The weights applied to all the data depended on the uncertainties of the observations, in accordance with the SARACEN method.<sup>5-7</sup>

**Methylphosphine–borane.** The refinement of the structure of methylphosphine–borane was conducted using a model of  $C_s$  symmetry. The model and method used were similar to those used for **1**, with full details, including the rotational constants used, given in the ESI.† The success of the final refinement, for which  $R_G = 0.100$  ( $R_D = 0.080$ ), can be assessed on the basis of the radial distribution curve (Fig. 3) and the molecular scattering intensity curves (Fig. S2).† The final refined parameters are listed in Table 4.



**Fig. 3** Experimental and difference (experimental–theoretical) radial distribution curve,  $P(r)/r$ , for methylphosphine–borane (**2**). Before Fourier inversion the data were multiplied by  $s \times \exp(-0.00002s^2)/(Z_C - f_C)(Z_P - f_P)$ .

## Discussion

The molecular structures of methylphosphine and methylphosphine–borane have been investigated in the gas phase by GED supplemented by *ab initio* calculations and rotational constants via the SARACEN method. An independent theoretical investigation of the structures was also undertaken.

The experimental structure of **1** is found to be generally in good agreement with both the theoretical structures and previous experimental results. For comparison, a selection of parameters from previous GED and MW studies are given in Table 5. It should be noted that neither the previous MW nor the earlier GED structure is complete, with each offering only a partial structure or requiring the use of fixed parameters.

The calculated structure was found to be generally independent of the level of theory and basis set used, with parameters generally varying by less than 1 pm in the case of the bond lengths or 1° for the angles, despite the wide range of calculations conducted. The largest deviations were observed for the P–C distance, which varied by 1.5 pm. Therefore, it can be stated that the molecule is adequately described by the MP2/6-311++G\*\* level of theory.

Comparing our experimental structure to the theoretical results, the P–C distance of 185.72(6) pm is in the middle of the range of the calculated values, closest to the MP2/6-311++G\*\* calculations.

**Table 4** Refined and calculated geometric parameters for methylphosphine-borane (**2**) from the GED study and microwave rotation constants, in MHz, used in the GED refinements<sup>a,b</sup>

Parameter	MP2/ 6-311++G**	SARACEN ( <i>r</i> <sub>hi</sub> )	Restraint	
<b>Independent parameters</b>				
<i>p</i> <sub>1</sub>	<i>r</i> P–C/ <i>r</i> P–B <sub>av.</sub> /pm	187.5	186.1(1)	—
<i>p</i> <sub>2</sub>	<i>r</i> P–C/ <i>r</i> P–B <sub>diff.</sub> /pm	5.4	5.0(2)	—
<i>p</i> <sub>3</sub>	<i>r</i> C–H/pm	109.2	108.7(5)	109.2(8)
<i>p</i> <sub>4</sub>	<i>r</i> P–H/pm	140.1	139.3(5)	140.1(8)
<i>p</i> <sub>5</sub>	<i>r</i> B–H/pm	120.8	119.9(5)	120.8(10)
<i>p</i> <sub>6</sub>	∠P–C–H <sub>av.</sub> /°	110.4	111.1(6)	110.5(10)
<i>p</i> <sub>7</sub>	∠P–C–H <sub>diff.</sub> /°	1.9	1.8(4)	1.9(4)
<i>p</i> <sub>8</sub>	∠P–B–H <sub>av.</sub> /°	104.7	106.2(5)	104.7(7)
<i>p</i> <sub>9</sub>	∠P–B–H <sub>diff.</sub> /°	1.4	1.3(5)	1.4(5)
<i>p</i> <sub>10</sub>	∠H(3)–C(1)–H(4)/°	109.5	110.2(8)	109.5(10)
<i>p</i> <sub>11</sub>	∠C–P–H/°	103.2	102.6(8)	103.2(10)
<i>p</i> <sub>12</sub>	∠C–P–B/°	115.0	115.0(1)	—
<i>p</i> <sub>13</sub>	∠H(9)–B(8)–H(10)/°	114.3	114.4(6)	114.3(7)
<i>p</i> <sub>14</sub>	∠H(7)–P(2)–H(6)/°	100.3	99.8(9)	100.3(10)
<b>Dependent parameters</b>				
<i>dp</i> <sub>1</sub>	<i>r</i> C(1)–P(2)/pm	182.1	181.1(2)	—
<i>dp</i> <sub>2</sub>	<i>r</i> P(2)–B(8)/pm	192.8	191.1(2)	—
<i>dp</i> <sub>3</sub>	∠P(2)–C(1)–H(3)/°	108.6	109.3(6)	—
<i>dp</i> <sub>4</sub>	∠P(2)–C(1)–H(4)/°	112.3	112.9(7)	—
<i>dp</i> <sub>5</sub>	∠P(2)–B(8)–H(11)/°	106.1	107.5(7)	—
<i>dp</i> <sub>6</sub>	∠P(2)–B(8)–H(10)/°	103.3	104.9(6)	—
<b>Rotational constants</b>				
Constant	Experimental	GED	Exp.–GED	Uncertainty
<i>C</i> <sub>z</sub> (I)– <i>A</i> <sub>z</sub> (I)	–12739.5	–12731.1	–8.4	12.8
<i>C</i> <sub>z</sub> (I)– <i>B</i> <sub>z</sub> (I)	–1011.7	–1011.3	–0.4	1.6
<i>C</i> <sub>z</sub> (I)	4985.8	4985.4	0.4	0.8
<i>C</i> <sub>z</sub> (II)– <i>A</i> <sub>z</sub> (II)	–12758.3	–12767.9	9.6	13.0
<i>C</i> <sub>z</sub> (II)– <i>B</i> <sub>z</sub> (II)	–1056.8	–1057.6	0.9	1.5
<i>C</i> <sub>z</sub> (I)– <i>C</i> <sub>z</sub> (II)	–151.9	–152.0	0.1	0.1
<i>C</i> <sub>z</sub> (III)– <i>A</i> <sub>z</sub> (III)	–12687.2	–12679.6	–7.6	12.5
<i>C</i> <sub>z</sub> (III)– <i>B</i> <sub>z</sub> (III)	–977.7	–976.9	–0.7	1.5
<i>C</i> <sub>z</sub> (I)– <i>C</i> <sub>z</sub> (III)	121.0	121.0	0.0	0.1

<sup>a</sup> Figures in parentheses are the estimated standard deviation of the last digits. <sup>b</sup> See text for parameter definitions.

The relatively small uncertainty of 0.06 pm on the experimental distance brings in to question the precision of the calculated distances, and no clear convergence is found as the level of theory and basis set is improved. The experimental distance is also comparable to the previous GED structure.

The P–H distance, which for this study is 142.1(1) pm, is in agreement with the largest calculated values, and is consistent with the value obtained from the previous GED study. The longest calculated bond lengths were obtained using correlation-consistent basis sets, with the P–H distance being 141.7 pm at CCSD(T)/aug-cc-pVQZ, and longer still when double- or triple-zeta basis sets are used. In contrast, the experimental C–H bond distances were found to agree with the shortest experimental bond lengths, corresponding to the MP2/aug-cc-pVQZ level of theory.

The remaining parameters, all bond angles, are found to be in good agreement with theoretical structures, although it must be noted that they all refer to the angles involving hydrogen atoms and theoretical restraints were used for some parameters. The H–P–H

**Table 5** A selection of structural parameters from previous GED<sup>11</sup> and MW<sup>12</sup> studies of methylphosphine (**1**) and a MW<sup>10</sup> study of methylphosphine-borane (**2**)<sup>a,b</sup>

Parameter	Previous GED	MW	This study
<b>Methylphosphine</b>			
<i>r</i> P–C/pm	185.8(3)	186.3 <sup>c</sup>	185.72(6)
<i>r</i> C–H/pm <sup>c</sup>	109.4(8)	109.3 <sup>c</sup>	108.0(1)
<i>r</i> P–H/pm	142.3(7)	141.4 <sup>c</sup>	142.1(1)
∠H–P–H/°	—	93.2 <sup>c</sup>	94.2(8)
∠C–P–H/°	96.5 <sup>d</sup>	—	97.4(8)
<b>Methylphosphine-borane</b>			
<i>r</i> P–C/pm	—	180.9(6)	181.1(2)
<i>r</i> P–B/pm	—	190.6(6)	191.1(2)
<i>r</i> P–H/pm	—	140.4(6)	139.3(5)
∠H–P–H/°	—	99.4(9)	99.8(9)
∠C–P–H/°	—	103.2(6)	102.6(8)
∠C–P–B/°	—	115.7(4)	115.0(1)

<sup>a</sup> Figures in parentheses are the estimated standard deviation of the last digits. <sup>b</sup> See text for parameter definitions. <sup>c</sup> In both studies the methyl group was assumed to possess local *C*<sub>3</sub> symmetry. <sup>d</sup> This parameter was fixed at this value and not allowed to refine. <sup>e</sup> No estimated standard deviations were reported for this study.

angle is found to be 94.2(8)°, significantly smaller than the 96.5° angle found in PH<sub>3</sub><sup>43</sup> and the >100° angle that is generally found in tertiary phosphines. The reduction in cone angle corresponds to an increase in *s* character in the phosphorus lone pair and a decrease in basicity, and is expected to lead to different properties when such molecules are used as ligands.<sup>1</sup>

The previous GED experiment assumed a fixed C–P–H angle of 96.5°, whilst the current study found the angle to be 97.4(8)°. The calculated angle was consistently around 97.5°. It is therefore likely that the previous study underestimated the C–P–H angle, which may have influenced the experimentally determined parameters. For **2**, a selection of structural parameters from a previous MW study is shown in Table 5. As was the case with **1**, the structure of **2** was found to be largely independent of the level of theory used. The only major exception to this is the P–B bond length, which varies by >2.5 pm across the range of calculations performed. This bond length is likely to be sensitive to the nature of the charge transfer from the phosphorus lone pair to the empty *p* orbitals of the boron atom, so it is understandable that the parameter is dependent on both the description of electron correlation employed, and the basis set used.

The experimental and computed structures show a good level of agreement. The P–B bond length is found by experiment to be 191.1(2) pm, a value which is consistent with the shortest of the calculated bond lengths, lying just below the MP2/6-311++G\*\* value. As both bond lengths calculated at the CCSD(T) level of theory deviated from the experimental value by a large amount, this result seems to suggest that the MP2 level of theory is better at predicting this bond length. The experimental P–C bond length is 181.1(2) pm, again at the shorter end of the theoretical values, closer to the values calculated at the MP2 level of theory.

For **1** the experimental P–H bond length was found to be closest to the longer theoretical distances, whereas in the complex the reverse is true. The distance from this study, 139.3(5) pm, is shorter

**Table 6** The changes in structural parameters defined as methylphosphine–borane (**2**) minus methylphosphine (**1**), from this study and *ab initio* calculations at the MP2/6–311++G\*\*, MP2/aug-cc-pVQZ, CCSD(T)/6–311++G\*\* and CCSD(T)/aug-cc-pVTZ levels of theory<sup>a,b</sup>

	This study <sup>c</sup>	MP2		CCSD(T)		Average from theory
		6–311++G**	aug-cc-pVQZ	6–311++G**	aug-cc-pVTZ	
rC(1)–H(3)/pm	0.7(5)	0.0	0.0	–0.1	–0.1	–0.05(5)
rC(1)–H(4)/pm	0.7(5)	0.0	0.0	0.0	0.0	0.0(0)
rC(1)–P(2)/pm	–4.6(2)	–3.5	–3.8	–3.8	–3.8	–3.7(2)
rP(2)–H(6)/pm	–2.8(5)	–0.9	–1.1	–1.2	–1.3	–1.1(2)
∠P(2)–C(1)–H(3)/°	–0.1(7)	–0.4	–0.5	–0.4	–0.4	–0.42(3)
∠P(2)–C(1)–H(4)/°	–1.2(9)	–1.5	–1.1	–1.4	–1.0	–1.3(3)
∠C(1)–P(2)–H(6)/°	5.2(11)	5.6	5.7	5.9	5.8	5.7(1)
∠H(6)–P(2)–H(7)/°	5.6(12)	5.8	6.3	6.0	6.5	6.1(3)

<sup>a</sup> Figures in parentheses are the estimated standard deviation of the last digits. For the theoretical average the standard deviation was calculated from the four sets of calculations shown. <sup>b</sup> See text for parameter definitions. <sup>c</sup> For the SARACEN refinement no distinction was made between rC(1)–H(3) and rC(1)–H(4).

than all the theoretical values and the value from the MW study, although this is only 1–2σ smaller than the calculated values at the MP2/6–311++G\*\* and MP2/aug-cc-pVQZ levels. The experimental B–H distance is again consistent with the shortest of the calculated values, being around 1σ from the computed value at the MP2/aug-cc-pVQZ level of theory.

The remaining experimental bond angles and torsion angles are all reasonably close to the calculated parameters, with the exception of the P–B–H bond angles, which are slightly larger than the calculations suggest.

To investigate the structural changes in **1** upon complexation to form **2**, the differences between comparable parameters were calculated. The changes in parameters from the SARACEN refinements and a selection of theoretical calculations are shown in Table 6.

Significant differences between the geometry of **1** and **2** are found, particularly around the phosphorus atom. The P–C bond is found to shorten by around 4 pm by both experiment and theory, whilst both the H(6)–P(2)–H(7) and C(1)–P(2)–H(6) angles increase by approximately 6°. This represents a move towards a more regular tetrahedral geometry, with the cone angles now found around phosphorus being close to those found in the more stable secondary and tertiary phosphines. (For example, the C–P–C angle in trimethylphosphine is 98°.)<sup>44</sup>

The borane group, previously having *D*<sub>3h</sub> symmetry, becomes pyramidal upon complexation and does not possess local *C*<sub>3v</sub> symmetry as the complex has overall *C*<sub>s</sub> symmetry. The B–H bond length is about 1.5 pm shorter in the adduct (based on the calculated B–H bond length in BH<sub>3</sub>), and the H–B–H angles reduce from 120° to around 114°. The newly formed P–B–H angles are around 107 and 104°.

The shortening of the P–H bond upon complexation, estimated by calculation to be 1.1(2) pm, is found to be 2.8(5) pm in this study. The experimentally determined P–H bond length was found to be at the longer end of the calculated bond lengths for **1** and at the shorter end for **2**; these results combine to produce the larger experimental change in bond length.

The P–C bond is found to shorten dramatically [–4.6(2) pm by experiment, –3.7(2) pm by theory] upon complexation. Such a shortening can be rationalised by considering charge transfer. The relative electronegativities of P and C (Pauling scale; C = 2.55, P = 2.19)<sup>45</sup> suggest the P–C bond is polarised such that the

C atom has a negative charge. When the P atom donates electron density to boron in **2** it must become more positive, and therefore more strongly bound to the negatively charged C, shortening the P–C bond.

The gas phase dissociation energy of methylphosphine–borane, defined as MePH<sub>2</sub>·BH<sub>3</sub> → BH<sub>3</sub> + MePH<sub>2</sub>, has been assessed at the MP2/6–311++G\*\* level of theory and was found to be 95 kJ mol<sup>–1</sup> at the MP2/6–311++G\*\* level of theory. The counterpoise method was used to account for BSSE and ZPE corrections were included.<sup>46,47</sup> For comparison, the same quantity in the nitrogen analogue, MeNH<sub>2</sub>·BH<sub>3</sub>, was previously estimated to be 146(3) kJ mol<sup>–1</sup>.<sup>48</sup> The enthalpy of formation, defined as ½B<sub>2</sub>H<sub>6</sub> + MePH<sub>2</sub> → MePH<sub>2</sub>·BH<sub>3</sub>, was calculated in the same way and found to be –27.8 kJ mol<sup>–1</sup>, whilst for MeNH<sub>2</sub>·BH<sub>3</sub> the value is –73(2) kJ mol<sup>–1</sup>.<sup>49</sup> The weaker bonding in the phosphine is expected due to its lower basicity.<sup>50</sup>

## Conclusion

Primary phosphines have received relatively little attention in the literature and are not widely used by chemists. However, complexation with borane results in a protected, less volatile compound which can be used in further synthesis more easily than the free phosphine. The complete gas-phase structures of methylphosphine and methylphosphine–borane have been determined for the first time and the structural changes that occur on complexation have been assessed. Large changes in geometry around the phosphorus atom are found, including a widening of the H–P–H angle and a shortening of the P–C bond upon complexation. The P–B distance is found to be 191.1(2) pm.

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