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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Supporting Information

Caution. Methylphosphine and diborane are pyrophoric and potentially highly toxic. All reactions and handling should be carried out in a well-ventilated hood..

Syntheses

Methylphosphine (**1**). The reducing agent ($LiAlH_4$, 1.68 g, 44 mmol) and tetraglyme (70 mL) were introduced in to a 250 mL flask under nitrogen. The flask was fitted on to a vacuum line containing two cells equipped with stopcocks. The flask was then immersed in a cold bath (273 K) and degassed. Dimethyl methylphosphonate [$MePO(OMe)_2$] (5.68 g, 37.4 mmol) diluted in tetraglyme (20 mL) was slowly added with a flex-needle through the septum over a time period of around 5 minutes. During and after the addition, the methylphosphine formed was distilled off under vacuum from the reaction mixture. A cold trap (193 K) selectively removed less volatile products and the methylphosphine was condensed in a second cold trap (77 K). At the end of the reaction, this second cell was disconnected from the vacuum line by stopcocks. Methylphosphine was thus obtained in 90 % yield (1.62 g, 33.7 mmol).

Diborane Orthophosphoric acid (60 mL of 85% aqueous solution) was introduced into a 500 mL two-necked flask equipped with a stirring bar and a cell containing potassium borohydride (3.2 g, 59 mmol). The flask was fitted on the vacuum line and degassed for 30 min. The potassium borohydride was added slowly in portions over about 1 hr. During and after addition, the diborane formed was distilled off under vacuum from the reaction mixture. A cold trap (193 K) selectively removed less volatile products and the diborane was condensed in a second cold trap (77 K). This second cell was disconnected from the vacuum line by stopcocks and kept at 77 K in a liquid nitrogen bath. Yield: 0.50 g (60%).

Methylphosphine-borane (**2**). In a Schlenk flask, diborane (about 1 g, 36 mmol) was added to methylphosphine (1.2 g, 25 mmol) diluted in 5 mL of pentane and cooled to 77 K. The reaction mixture was allowed to warm to room temperature and stirred for 5 min. at this temperature. The mixture was then distilled off on a vacuum line and the methylphosphine-borane was selectively condensed in a trap cooled at 203 K. This cell was then disconnected from the vacuum line by stopcocks and connected to the gas electron-diffraction apparatus. The methylphosphine-borane, obtained in essentially quantitative yield, is stable at room temperature for several months.

Experimental

Methylphosphine-borane The refinement of the structure of methylphosphine-borane was conducted using a model of C_s symmetry. Again it was found that the CH_3 group did not possess local C_3 symmetry, and neither did the BH_3 group. As before, the deviation in angles was modelled but the deviation in bond lengths was not, because calculated differences were very small. All C–H and all B–H bond lengths were thus assumed to be the equal. Fourteen independent geometric parameters were used to model the molecule, comprising five bond lengths and nine bond angles. The CH_3PH_2 fragment of **2** was described in the same way as **1**, with the exception that an average and difference were used to describe the P–C and P–B bond lengths (p_1, p_2). The unique parameters for **2** were B–H (p_5), C(1)–P(2)–B(8) (p_{12}), H(9)–B(8)–H(10) (p_{13}) and the two P(2)–B(8)–H bonds, for which an average and difference were used (p_8, p_9) such that P(2)–B(8)–H(11) = $p_8 + p_9$ and P(2)–B(8)–H(9) = $p_8 - p_9$. As for **1** additional parameters were available to allow for deviation from C_s symmetry in the form of H(4)–C(1)–P(2)–B(8) and C(1)–P(2)–B(8)–H(11) dihedral angles, but again neither of these parameters refined to a value that indicated a meaningful deviation from C_s symmetry, and so they were not included.

The starting parameters, amplitudes of vibration and curvilinear corrections were obtained in the same way as for **1**. All fourteen geometric parameters and eight groups of vibrational amplitudes were refined. Eleven geometric restraints (Table 4, main text) and six amplitude restraints (Table S9) were employed using the SARACEN method.[5–7] 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 (Figure 3, main text) and the molecular scattering intensity curves (Figure S2). Final refined parameters are listed in Table 4. The supporting data contains the interatomic distances and the corresponding amplitudes of vibration (Table S9), with the least-squares correlation matrix (Table S10) and the experimental coordinates from the GED analysis (Table S11).

A total of nine rotational constants for **2** were combined with the GED data.[10] These corresponded to the parent compound (labelled I) and the ^{13}C (II) and ^{10}B (III) isotopomers. Although microwave data were available for the deuterated species, these were not included in the refinement because C–D bond lengths and angles may differ from their C–H analogues and so the data are likely to introduce unknown errors in the structure. The rotational constants were corrected in the same way as for **1.** The corrected rotation constants were included in the refinements as the absolute value of C_z for the parent compound, the differences between C_z for the parent and isotopomers *i.e.* $C_z(\mathrm{I}) - C_z(\mathrm{II})$, $C_z(\mathrm{I}) - \mathrm{C}_z(\mathrm{III})$ and as differences between C_z and A_z/B_z for each isotopomer, *i.e.* $A_z(\mathrm{I}) - B_z(\mathrm{I})$, $A_z(\mathrm{I}) - C_z(\mathrm{I})$, $A_z(\mathrm{II}) - B_z(\mathrm{II})$ etc. These constants are given in Table 4 in the main text.

Table S1 Nozzle-to-plate distances (mm), weighting functions (nm^{-1}), correlation parameters, scale factors and electron wavelengths (pm) used in the gas electron diffraction study.

	Methylphosphine (**1**)		Methylphosphine-borane (**2**)	
Nozzle-to-plate distance[a]	127.8	284.6	92.0	249.5
Δs	2	2	2	2
s_{min}	80	20	90	30[c]
sw_1	120	60	120	60
sw_2	215	103	215	103
s_{max}	290	120	260	120
Correlation parameter	0.428	0.372	–0.014	0.332
Scale factor[b]	0.718(15)	0.794(6)	0.789(23)	0.697(17)
Electron wavelength	6.18	6.18	6.18	6.18

[a] Determined by reference to the scattering pattern of benzene vapour.

[b] Values in parentheses are the estimated standard deviations.

[c] Data below $s = 3$ nm^{-1} were cut due to the presence of dirt on the rotating sector.

Table S2 Molecular geometries of the lowest-energy structure of methylphosphine (**1**) conducted at the MP2 level of theory with the 6-31G*, 6-311G*, 6-311+G*, 6-311++G*, 6-311+G** and 6-311++G** basis sets.[a,b]

	MP2					
Parameter	6-31G*	6-311G*	6-311+G*	6-311++G*	6-311+G**	6-311++G**
*r*C(1)–H(3)	109.2	109.1	109.1	109.1	109.2	109.2
*r*C(1)–H(4)	109.1	109.0	109.0	109.0	109.1	109.1
*r*C(1)–P(2)	186.0	185.6	185.5	185.5	185.6	185.6
*r*P(2)–H(6)	141.6	141.6	141.7	141.7	141.1	141.0
∠P(2)–C(1)–H(3)	108.7	108.6	108.5	108.5	109.0	108.7
∠P(2)–C(1)–H(4)	113.7	113.9	114.0	114.0	113.8	113.8
∠H(3)–C(1)–H(4)	109.0	109.1	109.1	109.1	108.7	109.0
∠H(3)–C(1)–H(5)	107.5	107.3	107.3	107.3	107.5	107.5
∠C(1)–P(2)–H(6)	98.0	97.7	97.8	97.9	97.5	97.6
∠H(6)–P(2)–H(7)	94.8	94.6	94.7	95.0	94.4	94.6
Energy[c]	–381.7212	–381.7623	–381.7638	–381.7644	–381.8112	–381.8117
Relative energy[d]	237.6	129.6	125.8	124.3	1.2	0.0

[a] All distances in pm and angles in °.

[b] See Figure 1 for atom numbering.

[c] Energy in Hartrees.

Table S3 Molecular geometries of the lowest-energy structures of methylphosphine conducted at the MP2 and CCSD(T) levels of theory with the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets.[a,b]

	MP2			CCSD(T)		
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ[c]
*r*C(1)–P(2)	187.7	185.8	185.1	188.9	186.6	185.9
*r*C(1)–H(4)	109.8	108.6	108.5	110.2	109.0	108.9
*r*C(1)–H(3)	110.1	108.9	108.7	110.4	109.2	109.1
*r*P(2)–H(6)	142.8	141.4	141.1	143.5	142.0	141.7
∠P(2)–C(1)–H(4)	113.4	113.3	113.4	113.1	113.0	113.2
∠ P(2)–C(1)–H(3)	108.6	108.6	108.6	108.7	108.6	108.6
∠C(1)–P(2)–H(6)	97.4	97.7	97.8	97.1	97.5	97.6
∠H(3)–C(1)–H(4)	109.1	109.3	109.2	109.1	109.3	109.2
∠H(3)–C(1)–H(5)	107.7	107.8	107.7	107.9	107.9	107.8
∠H(6)–P(2)–H(7)	93.5	93.5	93.5	93.3	93.3	93.3

[a] All distances in pm and angles in °. [b] See Figure 1 for atom numbering. [c] Extrapolated as CCSD(T)/aug-cc-pVQZ = CCSD(T)/aug-cc-pVTZ + [MP2/aug-cc-pVQZ – MP2/aug-cc-pVTZ]

Table S4 Molecular geometries of the lowest-energy structure of methylphosphine-borane (**2**) calculated at the MP2 level of theory with the 6-31G*, 6-311G*, 6-311+G*, and 6-311++G** basis sets.[a,b]

	MP2			
Parameter	6-31G*	6-311G*	6-311+G*	6-311++G**
*r*C(1)–H(3)	109.2	109.1	109.1	109.2
*r*C(1)–H(4)	109.1	109.0	109.0	109.1
*r*C(1)–P(2)	182.7	182.1	182.1	182.1
*r*P(2)–H(6)	140.6	140.5	140.6	140.1
*r*P(2)–B(8)	193.4	192.5	192.5	192.8
*r*B(8)–H(9)	121.0	121.2	121.2	120.9
*r*B(8)–H(11)	120.8	120.9	120.9	120.6
∠P(2)–C(1)–H(3)	109.4	109.3	109.3	109.6
∠P(2)–C(1)–H(4)	112.4	112.5	112.6	112.3
∠H(3)–C(1)–H(4)	108.1	108.0	107.9	108.2
∠H(3)–C(1)–H(5)	108.7	108.8	108.8	108.6
∠C(1)–P(2)–H(6)	103.0	103.3	103.4	103.2
∠H(6)–P(2)–H(7)	100.0	100.3	100.3	100.3
∠C(1)–P(2)–B(8)	115.4	115.4	115.1	115.0
∠P(2)–B(8)–H(9)	103.6	104.1	103.9	103.3

∠P(2)–B(6)–H(11)	106.0	106.2	106.4	106.1
∠H(9)–B(8)–H(10)	113.7	113.5	113.5	113.7
∠H(9)–B(8)–H(11)	114.2	113.9	113.9	114.3
ϕH(3)–C(1)–P(2)–H(6)	51.8	52.1	52.1	52.1
Energy[c]	–408.2317	–408.2847	–408.2868	–408.3568
Relative energy[d]	328.5	189.3	183.8	0.0

[a] All distances in pm and angles and dihedral angles in °.

[b] See Figure 1 for atom numbering.

[c] Energy in Hartrees.

[d] Energy in kJ mol^{-1} relative to the MP2/6-311++G** level of theory.

Table S5 Molecular geometries of the lowest-energy structures of methylphosphine-borane conducted at the MP2 and CCSD(T) levels of theory with the aug-cc-pVDZ, aug-cc-pVTZ and aug-cc-pVQZ basis sets.[a,b]

	MP2			CCSD(T)		
	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ[c]
*r*C(1)–P(2)	183.8	181.9	181.3	184.8	182.8	182.2
*r*C(1)–H(4)	109.8	108.7	108.5	110.2	109.0	108.9
*r*C(1)–H(3)	110.0	108.8	108.7	110.4	109.1	109.0
*r*P(2)–H(6)	141.7	140.3	140.0	142.2	140.7	140.5

*r*P(2)–B(8)	194.9	192.2	191.4	196.3	193.3	192.5
*r*B(8)–H(9)	122.1	120.7	120.5	122.5	121.2	121.1
*r*B(8)–H(10)	121.7	120.3	120.2	122.2	120.7	120.6
∠P(2)–C(1)–H(3)	108.1	108.0	108.1	108.2	108.2	108.3
∠P(2)–C(1)–H(4)	112.4	112.3	112.4	112.2	112.0	112.0
∠C(1)–P(2)–H(6)	103.3	103.5	103.5	103.2	103.3	103.4
∠C(1)–P(2)–B(8)	114.3	114.5	114.5	114.8	114.7	114.7
∠H(6)–P(2)–H(7)	99.7	99.7	99.8	99.5	99.6	99.7
∠P(2)–B(8)–H(9)	102.6	102.7	102.8	102.8	102.8	102.9
∠H(3)–C(1)–H(4)	109.8	110.0	109.9	109.8	110.0	109.9
∠H(3)–C(1)–H(5)	108.4	108.4	108.3	108.4	108.5	108.4
∠H(9)–B(8)–H(10)	113.9	113.9	113.8	114.1	113.8	113.7
∠H(9)–B(8)–H(11)	114.8	114.7	114.7	114.7	114.7	114.7
∠P(2)–B(6)–H(11)	106.1	106.1	106.3	105.7	106.2	106.4

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[a] All distances in pm and angles in °. [b] See Figure 1 for atom numbering. [c] Extrapolated as CCSD(T)/aug-cc-pVQZ = CCSD(T)/aug-cc-pVTZ + [MP2/aug-cc-pVQZ – MP2/aug-cc-pVTZ].

Table S6 Interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of methylphosphine.[a,b]

	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	C(1)–H(4)	107.6(1)	0.088(2)	0.76(8)
u_2	C(1)–H(3)	107.6(1)	0.088(tied to u_1)	—
u_3	C(1)–H(5)	107.6(1)	0.088(tied to u_1)	—
u_4	C(1)–P(2)	185.60(6)	0.049(2)	—
u_5	P(2)–H(6)	142.0(1)	0.074(3)	—
u_6	P(2)–H(7)	142.0(1)	0.074(tied to u_5)	—
u_7	C(1)···H(6)	247.2(15)	0.130(tied to u_{15})	—
u_8	C(1)···H(7)	247.2(15)	0.130(tied to u_{15})	—
u_9	H(4)···H(3)	174.8(10)	0.123(fixed)	—
u_{10}	H(4)···H(5)	174.8(10)	0.123(fixed)	—
u_{11}	H(4)···P(2)	249.2(8)	0.114(tied to u_{15})	—
u_{12}	H(4)···H(6)	268.3(15)	0.204(fixed)	—
u_{13}	H(4)···H(7)	268.3(15)	0.204(fixed)	—
u_{14}	H(3)···H(5)	171.1(17)	0.124(fixed)	—
u_{15}	H(3)···P(2)	242.9(6)	0.118(3)	—
u_{16}	H(3)···H(6)	339.0(10)	0.221(fixed)	—
u_{17}	H(3)···H(7)	280.3(12)	0.139(fixed)	—
u_{18}	H(5)···P(2)	242.9(6)	0.118(tied to u_{15})	—
u_{19}	H(5)···H(6)	280.3(12)	0.139(fixed)	—
u_{20}	H(5)···H(7)	338.9(10)	0.221(fixed)	—
u_{21}	H(6)···H(7)	207.1(14)	0.144(fixed)	—

[a] Estimated standard deviations, obtained in the least squares refinement, are given in parentheses. [b] Amplitudes not refined were fixed at the values obtained using the MP2/6-311++G** force field.

Table S7 Least-squares correlation matrix (× 100) for methylphosphine.[a]

	p_6	p_7	p_8	u_5	k_2
p_4	–62	–91			
p_6	100	62	76		
u_4				52	84
u_5				100	62

[a] Only elements with absolute values > 50% are shown; k_2 is a scale factor.

Table S8 Experimental gas-phase electron diffraction coordinates of methylphosphine (in pm).

Atom	x	y	z
C(1)	185.72	0.00	0.00
P(2)	0.00	0.00	0.00
H(3)	221.56	54.53	–86.06
H(4)	229.82	–98.59	0.00
H(5)	221.56	54.53	86.06
H(6)	–18.26	–94.98	104.04
H(7)	–18.26	–94.98	–104.04

Table S9 Interatomic distances (r_a/pm) and amplitudes of vibration (u_{h1}/pm) for the restrained GED structure of methylphosphine-borane.[a,b]

	Atom pair	r_a/pm	u_{h1}/pm[b]	Restraint
u_1	C(1)–H(4)	108.4(5)	0.083(5)	0.076(8)
u_2	C(1)–H(3)	108.4(5)	0.083(tied to u_1)	—
u_3	H(11)–B(8)	119.9(5)	0.064(6)	0.085(10)
u_4	H(9)–B(8)	119.9(5)	0.064(tied to u_3)	—
u_5	P(2)–H(6)	139.0(5)	0.093(5)	0.082(8)
u_6	H(3)···H(5)	170.8(29)	0.124(fixed)	—
u_7	H(4)···H(3)	177.3(12)	0.123(fixed)	—
u_8	C(1)–P(2)	181.0(2)	0.064(3)	0.050(6)
u_9	P(2)–B(8)	191.0(2)	0.062(3)	—
u_{10}	H(9)···H(10)	195.2(23)	0.136(fixed)	—
u_{11}	H(11)···H(9)	200.5(12)	0.136(fixed)	—
u_{12}	H(6)···H(7)	212.0(14)	0.140(fixed)	—
u_{13}	H(3)···P(2)	239.3(10)	0.108(5)	—
u_{14}	H(2)···P(5)	244.0(10)	0.105(tied to u_{13})	—
u_{15}	P(2)···H(9)	248.9(10)	0.129(tied to u_{13})	—
u_{16}	C(1)···H(6)	250.5(12)	0.116(fixed)	—
u_{17}	P(2)···H(11)	252.9(12)	0.128(tied to u_{13})	—
u_{18}	H(4)···H(6)	274.3(20)	0.215(fixed)	—
u_{19}	H(6)···B(8)	285.5(11)	0.127(12)	0.137(14)
u_{20}	H(3)···H(7)	341.8(12)	0.223(fixed)	—
u_{21}	H(3)···H(10)	358.2(12)	0.358(fixed)	—
u_{22}	H(6)···H(9)	309.2(17)	0.248(fixed)	—
u_{23}	H(6)···H(8)	311.6(20)	0.245(fixed)	—
u_{24}	C(1)···B(8)	313.1(1)	0.129(7)	0.117(11)
u_{25}	C(1)···H(9)	328.1(10)	0.251(tied to u_{24})	—
u_{26}	H(3)···B(8)	330.0(10)	0.233(tied to u_{24})	—
u_{27}	H(3)···H(6)	281.9(20)	0.137(fixed)	—
u_{28}	H(3)···H(9)	301.3(12)	0.370(fixed)	—
u_{29}	H(6)···H(10)	369.3(11)	0.145(fixed)	—
u_{30}	H(2)···B(11)	405.7(7)	0.127(fixed)	—

u_{31}	C(1)···H(11)	408.6(9)	0.125(fixed)	—
u_{32}	H(4)···H(9)	424.8(10)	0.257(fixed)	—
u_{33}	H(3)···H(11)	433.0(10)	0.222(fixed)	—
u_{34}	H(2)···H(8)	489.9(11)	0.157(fixed)	—

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[a] Estimated standard deviations, obtained in the least-squares refinement, are given in parentheses.

[b] Amplitudes not refined were fixed at the values obtained using the MP2/6-311++G** force field.

Table S10 Least-squares correlation matrix (×100) for methylphosphine-borane.[a]

	p_3	p_5	p_9	p_{11}	p_{12}	u_1	u_3	u_5	u_8	u_9	u_{13}	k_1	k_2
p_1							56						
p_2	-63	-50		-83									
p_3	100			67									
p_4			66						-54	-64	-57		
p_5		100		55		-68							
p_6					-81						59		
p_8				53									
p_{12}					100						-62		
u_3							100	58					
u_8									100	74	58	75	62
u_9										100	57	64	50
k_1												100	55

[a] Only elements with absolute values ≥ 50% are shown; k_1 and k_2 are scale factors.

Table S11 Experimental gas-phase electron diffraction coordinates of methylphosphine-borane (in pm).

Atom	*x*	*y*	*z*
C(1)	0.00	0.00	0.00
P(2)	0.00	–181.11	0.00
H(3)	–85.91	35.99	56.01
H(4)	0.00	42.34	–100.10
H(5)	85.91	35.99	56.01
H(6)	106.52	–211.41	–84.45
H(7)	–106.52	–211.41	–84.45
B(8)	0.00	–261.95	173.10
H(9)	98.12	–219.18	227.05
H(10)	–98.12	-219.18	227.05
H(11)	0.00	–380.78	157.35

Figure S1 Experimental and final weighted difference (experimental – theoretical) molecular-scattering intensities for methylphosphine.

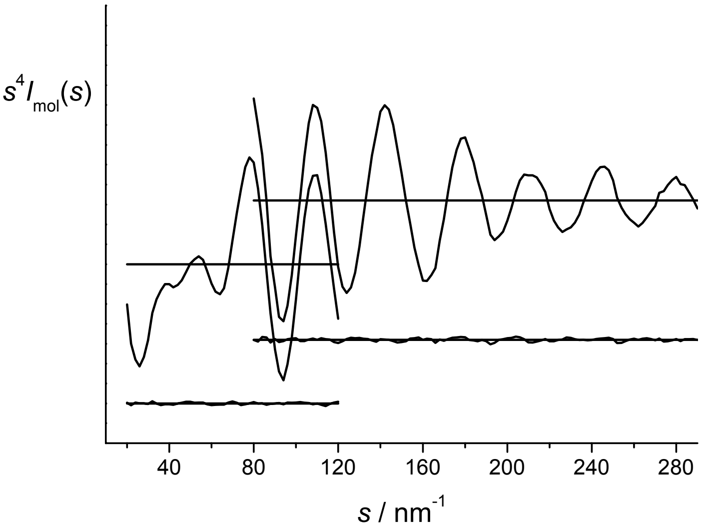

Figure S2 Experimental and final weighted difference (experimental – theoretical) molecular-scattering intensities for methylphosphine-borane.