

Phosphanylborohydrides: First Assessment of the Relative Lewis Basicities of $[\text{BH}_3\text{PPh}_2]^-$, CH_3PPh_2 , and HPPH_2

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The compounds $\text{K}[\text{PPh}_2]$, HPPH_2 , CH_3PPh_2 , $\text{BH}_3(\text{H})\text{PPh}_2$, $\text{BBr}_3(\text{H})\text{PPh}_2$, $\text{BH}_3(\text{CH}_3)\text{PPh}_2$, $\text{BBr}_3(\text{CH}_3)\text{PPh}_2$, $[\text{H}_2\text{PPh}_2]\text{I}$, $[\text{CH}_3(\text{H})\text{PPh}_2]\text{I}$, $[(\text{CH}_3)_2\text{PPh}_2]\text{I}$, and $\text{K}[(\text{BH}_3)_2\text{PPh}_2]$ have been investigated by NMR spectroscopy. In addition, X-ray crystal structures have been determined for $\text{K}(18\text{-crown-6})[\text{PPh}_2]$, $\text{BBr}_3(\text{H})\text{PPh}_2$, $\text{BBr}_3(\text{CH}_3)\text{PPh}_2$, $[\text{H}_2\text{PPh}_2]\text{I}$, $[\text{CH}_3(\text{H})\text{PPh}_2]\text{I}$, $[(\text{CH}_3)_2\text{PPh}_2]\text{I}$, and $\text{K}(18\text{-crown-6})[(\text{BH}_3)_2\text{PPh}_2]$. An evaluation of coupling constants (e.g. $^1J_{\text{PCi}}$; C_i = *ipso* carbon atom of a phenyl ring) augmented by an inspection of key structural parameters (e.g. the angles $C_i\text{--P--}C_i'$) leads to the con-

clusion that dative bonds originating from ligand $[\text{BH}_3\text{PPh}_2]^-$ possess a significantly higher p character than dative bonds involving the ligands HPPH_2 and CH_3PPh_2 . The $^1J_{\text{PB}}$ values obtained for $\text{BH}_3(\text{H})\text{PPh}_2$, $\text{BH}_3(\text{CH}_3)\text{PPh}_2$, and $[(\text{BH}_3)_2\text{PPh}_2]^-$ suggest $[\text{BH}_3\text{PPh}_2]^-$ to form the strongest $[\text{BH}_3]$ adduct of all three compounds which is in agreement with the results of displacement reactions employing the couples $\text{CH}_3\text{PPh}_2/[(\text{BH}_3)_2\text{PPh}_2]^-$ and $[\text{BH}_3\text{PPh}_2]^-/\text{BH}_3(\text{CH}_3)\text{PPh}_2$.

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Introduction

Organophosphanes have been extensively studied as ligands to both main group Lewis acids and transition metals in order to unveil the factors governing the stability and reactivity of coordination complexes.^[1] In the course of these studies it soon became apparent that phosphanes may not generally be viewed as simple σ donors because often an intricate interplay exists between the $\text{P} \rightarrow \text{M}$ σ interaction and an $\text{M} \rightarrow$ ligand π back-donation. The π acceptor strength of PF_3 , for example, is comparable to that of CO , commonly regarded as the archetypical π acceptor ligand. If, on the other hand, electropositive substituents are attached to the phosphorus atom, one would expect an increase in Lewis basicity likely together with a decrease in π acidity of the respective phosphane molecule. One way to test this assumption is through replacement of alkyl groups on phosphorus by borane moieties. Using parent $[\text{BH}_3]$, we thereby arrive at a class of anionic species $[\text{BH}_3\text{PRR}']^-$ which are the heavier homologues of the better-known aminoborohydrides $[\text{BH}_3\text{NRR}']^-$.^[2] Until today, phosphanylborohydrides $[\text{BH}_3\text{PRR}']^-$ have mainly been generated in situ and used as building blocks for the preparation of chiral organophosphanes.^[3–6] Moreover, aiming at the synthesis of polymeric materials involving group 13 and group 15

elements, Manners and co-workers have recently employed the compound $\text{Li}[\text{BH}_3\text{PPh}_2]$ in the preparation of linear hybrid aminoborane/phosphanylborane chains.^[7] The same group has also reported on the synthesis of the platinum phosphanylborohydride complexes *trans*- $[\text{PtH}(\text{BH}_3\text{PPh}_2)(\text{PEt}_3)_2]$ ($\text{R} = \text{H}, \text{Ph}$) by the regioselective insertion of the $\text{Pt}(\text{PEt}_3)_2$ fragment into the P--H bond of $\text{BH}_3(\text{H})_2\text{PPh}$ or $\text{BH}_3(\text{H})\text{PPh}_2$.^[8] Other examples of structurally characterised phosphanylborohydride complexes include the compounds $[(\text{dppp})\text{Pd}(\text{C}_6\text{F}_5)(\text{BH}_3\text{PPh}_2)]^{[9]}$ and $[(\text{C}_5\text{Me}_5)\text{Fe}(\text{CO})_2(\text{BH}_3\text{PPh}_2)]^{[10]}$. Finally, Müller et al. have explored the complexation potential of $[\text{BH}_3\text{P}(\text{CH}_3)_2]^-$ and $[\text{BH}_3\text{P}(\text{Ph})\text{tBu}]^-$ toward lithium and aluminium.^[11]

In a 1996 paper, Fu et al. described diphenylphosphido-boratabenzene, $[(\text{BC}_5\text{H}_5)\text{PPh}_2]^-$, as anionic analogue of the ubiquitous triphenylphosphane ligand and explored its coordination chemistry.^[12] Stimulated by their investigations, our group embarked on a systematic study of the ligand properties of anionic phosphanylborohydrides $[\text{BH}_3\text{PRR}']^-$ in comparison to their neutral isoelectronic and isostructural methyl analogues $\text{CH}_3\text{PRR}'$. For a start, we are focusing on compounds in which the phosphorus atom is exclusively engaged in σ bonds. Effects of π bonding will be considered at a later stage. All compounds under investigation here are based on the PPh_2 fragment (Figure 1). The series of derivatives starts with the $[\text{PPh}_2]^-$ ion ($\text{K}[\text{PPh}_2]$, **1**) and continues with the phosphanes HPPH_2 (**2**) and H_3CPPh_2 (**3**), followed by their complexes with the main group Lewis acids $[\text{BH}_3]$, H^+ , and $[\text{CH}_3]^+$ (cf. **4H**, **5H**, and **6–8**). As we were not able to grow X-ray quality crystals of the $[\text{BH}_3]$ adducts **4H** and **5H**, the corresponding BBr_3 ad-

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ducts **4Br** and **5Br** were structurally characterised instead. The series closes with the anionic species $K[(BH_3)_2PPh_2]$ (**9**).

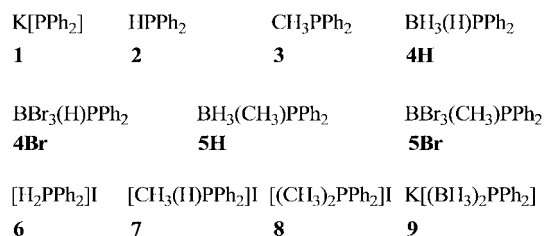


Figure 1. The potassium phosphide **1**, the phosphanes **2**, **3**, and the phosphane adducts **4–9**.

With this selection of molecules it is possible to study systematic trends in NMR- and structural parameters (i) upon increasing the coordination number of phosphorus from two to three and four (e.g. $[PPh_2]^-$ vs. $HPPH_2$ vs. $[H_2PPh_2]^+$) and (ii) by comparing isoelectronic and isostructural species of different charge (e.g. $[(BH_3)_2PPh_2]^-$ vs. $[(CH_3)_2PPh_2]^+$). It is to be mentioned that some of the compounds under investigation here are already known in the literature (see below). However, crystal structure analyses were missing and even though selected NMR spectroscopic data have been reported, measurement conditions vary to such an extent that a re-investigation using the same solvent and (in the case of **6–8**) counterion was inevitable, because these can greatly influence the chemical shift values.^[13]

Results and Discussion

Syntheses: $K[PPh_2]$ (**1**) was prepared through deprotonation of $HPPH_2$ (**2**) with potassium metal in THF. $BH_3(H)PPh_2$ (**4H**) is accessible from $HPPH_2$ (**2**) and B_2H_6 .^[14] However, we preferred to use a calibrated solution of $BH_3 \cdot THF$ in THF which is more convenient to handle. $BBr_3(H)PPh_2$ (**4Br**) was synthesised from $HPPH_2$ (**2**) and BBr_3 following a published procedure.^[14] $BH_3(CH_3)PPh_2$ (**5H**) is formed similar to $BH_3(H)PPh_2$ (**4H**) upon treatment of CH_3PPh_2 (**3**) with $BH_3 \cdot THF$ in THF (Manners et al. have used $BH_3 \cdot SMe_2$ instead^[7]). An alternative route to **5H** employs $ClPPh_2$ as starting material which is first methylated with $MeMgI$ and subsequently borylated with $NaBH_4/I_2$.^[15] $BBr_3(CH_3)PPh_2$ (**5Br**) was synthesised from CH_3PPh_2 (**3**) and BBr_3 following a published procedure.^[16] The phosphonium iodide salts $[H_2PPh_2]I$ (**6**) and $[CH_3(H)PPh_2]I$ (**7**) were

prepared by treatment of $HPPH_2$ (**2**) and CH_3PPh_2 (**3**) with excess HI in toluene; for the syntheses of $[CH_3(H)PPh_2]Br$ and $[(CH_3)_2PPh_2]I$ (**8**) see refs.^[17,18] The synthesis of $K[(BH_3)_2PPh_2]$ was accomplished by deprotonation of $BH_3(H)PPh_2$ (**4H**) with KH and subsequent addition of $BH_3 \cdot THF$ in THF.

In the following, all compounds under investigation will be viewed as adducts between the Lewis bases $HPPH_2$ (**2**), CH_3PPh_2 (**3**), and $[BH_3PPh_2]^-$ with the Lewis acids H^+ , $[BH_3]$, BBr_3 , and $[CH_3]^+$.

X-ray Crystallography: Single crystals of the potassium salts **1** and **9** were obtained only after potassium complexation with 18-crown-6. The compounds $K(18\text{-crown-6})[PPh_2]$ and $K(18\text{-crown-6})[(BH_3)_2PPh_2]$ will be referred to as **1^c** and **9^c**, respectively. Selected bond lengths and angles of compounds **1^c**, **4Br**, **5Br**, **6**, **7**, **8**, and **9^c** are compiled in Table 1.

The potassium diphenylphosphide $K(18\text{-crown-6})[PPh_2]$ (**1^c**) crystallises from THF in the monoclinic space group $P2_1/n$ (Figure 2).

The asymmetric unit of **1^c** contains two formula units and features diphenylphosphide anions in distinctly different chemical environments: The first $[PPh_2]^-$ fragment coordinates to two potassium counterions with bond lengths $P(1)-K(1)$ and $P(1)-K(1A)$ of 3.347(1) Å and 3.267(1) Å, respectively (sum of the ionic radius of K^+ and the van-der-Waals radius of phosphorus: 3.55 Å^[19]). Each potassium centre is encapsulated by one crown ether ligand; in addition, a relatively short intermolecular contact is established between $K(1A)$ and one phenyl ring [$K(1A) \cdots C(25A) = 3.518(2)$ Å]. The bond angles around the phosphorus atom $P(1)$ cover the wide range from 84.0(1)° for $C(21)-P(1)-K(1A)$ to 150.1(1)° for $K(1)-P(1)-K(1A)$. However, the angle defined by the two phenyl *ipso*-carbon atoms and the phosphorus atom is close to the ideal tetrahedral angle of 109.5° [$C(21)-P(1)-C(31) = 107.1(1)^\circ$]. A largely two-coordinate phosphorus atom is found in the second $[PPh_2]^-$ ion [shortest $P(1A) \cdots K$ contact: 5.918 Å]. Nevertheless, both the $P-C_i$ bond lengths ($C_i = ipso$ carbon atom of a phenyl ring) and the C_i-P-C_i' bond angles of the two different PPh_2 fragments are almost identical within experimental error [$C(21A)-P(1A)-C(31A) = 108.3(1)^\circ$; Table 1]. Two other adducts of $K[PPh_2]$ have previously been characterised, the N,N,N',N'',N''' -pentamethyldiethylenetriamine complex $\{K(pmdta)[PPh_2]\}_n$ ^[20] and the 1,4-dioxane complex $\{K(dioxane)_2[PPh_2]\}_n$.^[21] Most notably, Eaborn, Smith

Table 1. Key structural parameters of compounds **1^c**, **4Br**, **5Br**, **6**, **7**, **8**, and **9^c**.

		P–B	P–C _i	P–CH ₃	C _i –P–C _i '
1^c	$K(18\text{-c-6})[PPh_2]$	–	1.811(2)/1.815(2) ^[a]	–	107.1(1) ^[a]
		–	1.807(2)/1.817(2) ^[b]	–	108.3(1) ^[b]
4Br	$BBr_3(H)PPh_2$	1.965(4)	1.803(4)/1.805(4)	–	110.8(2)
5Br	$BBr_3(CH_3)PPh_2$	1.976(9)	1.801(11)/1.810(10)	1.814(11)	106.5(5)
6	$[H_2PPh_2]I$	–	1.794(2)/1.798(2)	–	109.6(1)
7	$[CH_3(H)PPh_2]I$	–	1.796(3)/1.797(3)	1.798(3)	110.8(1)
8^[18]	$[(CH_3)_2PPh_2]I$	–	1.794(3)	1.782(3)	107.6(2)
9^c	$K(18\text{-c-6})[(BH_3)_2PPh_2]$	1.930(2)/1.940(2)	1.829(2)/1.831(2)	–	100.2(1)

[a] Coordinated $[PPh_2]$ unit. [b] Non-coordinated $[PPh_2]$ unit.

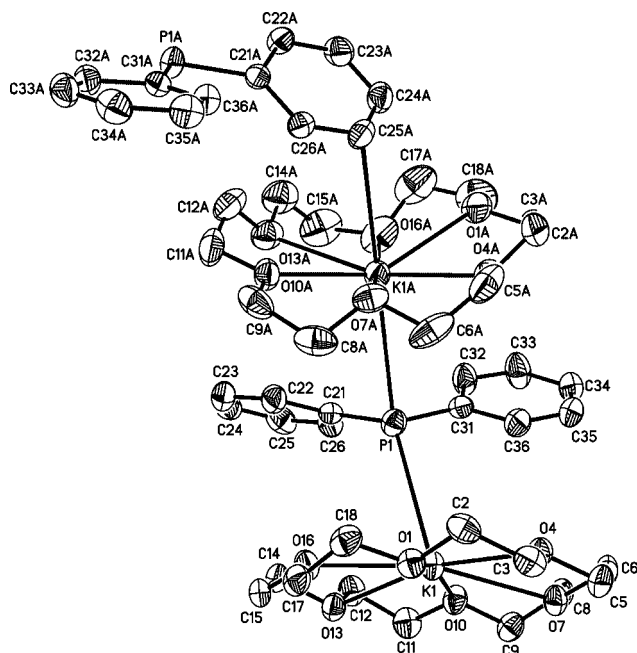


Figure 2. Molecular structure and numbering scheme of compound **1c**; thermal ellipsoids shown at the 50% probability level; hydrogen atoms omitted for clarity. Selected bond lengths [Å] and bond angles [°]: P(1)–C(21) = 1.815(2), P(1)–C(31) = 1.811(2), P(1A)–C(21A) = 1.817(2), P(1A)–C(31A) = 1.807(2), P(1)–K(1) = 3.347(1), P(1)–K(1A) = 3.267(1), K(1A)···C(25A) = 3.518(2); C(21)–P(1)–K(1A) = 84.0(1), K(1)–P(1)–K(1A) = 150.1(1), C(21)–P(1)–C(31) = 107.1(1), C(21A)–P(1A)–C(31A) = 108.3(1).

et al.^[22] have determined the crystal structure of solvent-free $\{\text{K}[\text{PPh}_2]\}_n$ which contains seven molecules in the asymmetric unit.

ORTEP drawings of the molecular structures of the boron–phosphorus adducts $(\text{BBr}_3)\text{HPPH}_2$ (**4Br**) and $\text{BBr}_3(\text{CH}_3)\text{PPh}_2$ (**5Br**) as well as of the phosphonium salts $[\text{H}_2\text{PPh}_2]\text{I}$ (**6**), $[\text{CH}_3(\text{H})\text{PPh}_2]\text{I}$ (**7**), and $[(\text{CH}_3)_2\text{PPh}_2]\text{I}$ (**8**)^[18,23] can be found in the Supporting Information. In all these compounds, the phosphorus atom is surrounded by four substituents. Important bond lengths and angles for comparison are listed in Table 1. In the case of **6** and **7**, the iodide ions are part of a complex network of P–H···I and Ph–H···I hydrogen bridges.

The phosphanylborohydride adduct $\text{K}(\text{18-crown-6})\text{--}[(\text{BH}_3)_2\text{PPh}_2]$ (**9c**) crystallises in the monoclinic space group $P2_1/c$ (Figure 3).

Each K^+ ion is complexed by six oxygen atoms of a crown ether molecule and establishes two short and one significantly longer contact to the hydrogen atoms of one $[\text{BH}_3]$ fragment [$\text{K}(1)\text{--H}(1\text{A}) = 2.683 \text{ Å}$, $\text{K}(1)\text{--H}(1\text{C}) = 3.003 \text{ Å}$, $\text{K}(1)\cdots\text{H}(1\text{B}) = 3.452 \text{ Å}$]. Using Edelstein's correlation^[24] of metal–boron distances as a measure of the denticity of borohydride groups, values of $1.6 \pm 0.1 \text{ Å}$ and $1.36 \pm 0.06 \text{ Å}$ are estimated for the ionic radii of bidentate and tridentate borohydride ligands, respectively. Thus, $\text{B}\cdots\text{K}$ distances of about 3.25 Å and 3.01 Å are to be expected for $\text{K}\text{--}\mu_2\text{--BH}_3\text{R}$ and $\text{K}\text{--}\mu_3\text{--BH}_3\text{R}$ coordination modes (ionic radius of octacoordinated $\text{K}^+ = 1.65 \text{ Å}$ ^[25]). Since the $\text{B}(1)\cdots$

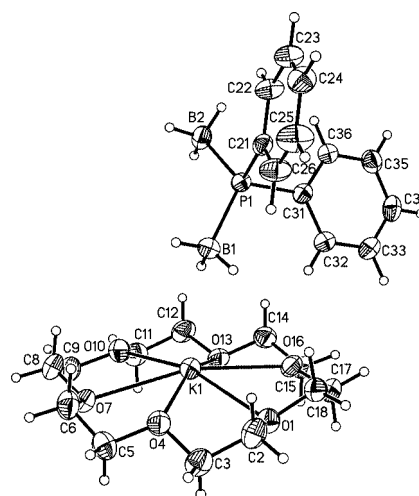
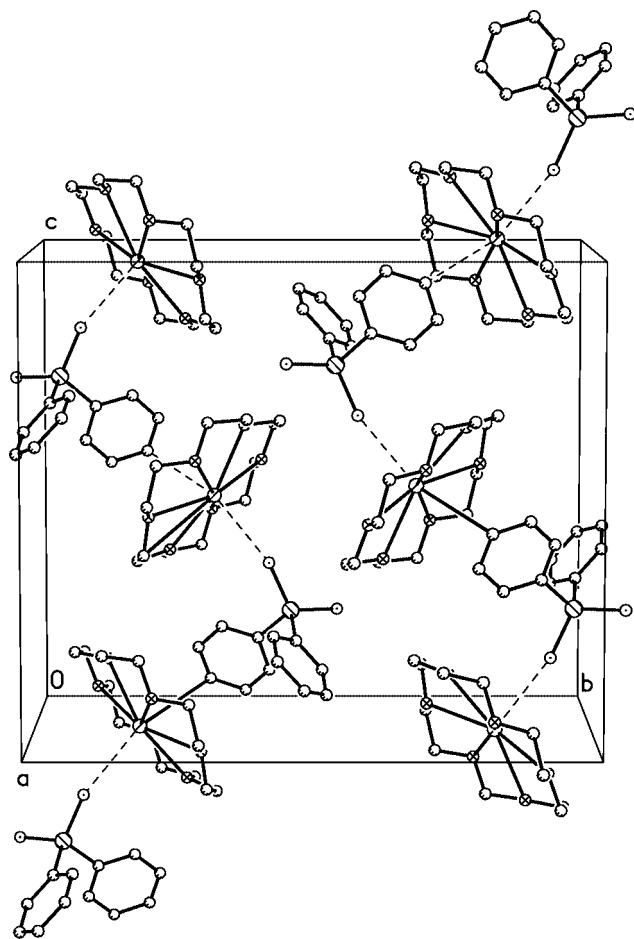


Figure 3. Molecular structure and numbering scheme of compound **9c**; thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: P(1)–B(1) = 1.930(2), P(1)–B(2) = 1.940(2), P(1)–C(21) = 1.829(2), P(1)–C(31) = 1.831(2), C(34)–K(1)[#] = 3.372(2), K(1)–H(1A) = 2.683, K(1)···H(1B) = 3.452, K(1)–H(1C) = 3.003, B(1)···K(1) = 3.205; B(1)–P(1)–B(2) = 116.3(1), C(21)–P(1)–C(31) = 100.2(1). Symmetry transformation used to generate equivalent atoms: $x, -y + 1/2, z - 1/2$ (#).

K(1) distance in **9c** amounts to 3.205 Å , it may be concluded that $[(\text{BH}_3)_2\text{PPh}_2]^-$ acts as bidentate ligand toward the potassium cation which is the most common binding mode in metal borohydrides.^[24] Further short contacts between the phenyl carbon atom C(34) and the neighbouring potassium ion K(1)[#] [$\text{C}(34)\text{--K}(1)^{\#} = 3.372(2) \text{ Å}$] stabilize the molecular packing as zig-zag chains in the crystal lattice (Figure 4).

Looking at the series of compounds **1c**, **4Br**, **5Br**, **6**, **7**, **8**, and **9c**, it is our goal to find out whether differences in the electron-density distribution at phosphorus can be correlated to systematic trends in the key structural parameters of these molecules (cf. Table 1). To this end we are considering the P–C_i bond lengths and the C_i–P–C_i' bond angles of the PPh_2 fragments first. According to Bent's rule,^[26] a tetracoordinate atom A directs hybrids of greater p character toward more electronegative substituents S and S' which in turn leads to smaller S–A–S' bond angles. In this context, lone pairs on atoms not involved in multiple bonds are in a first approximation viewed as residing in tetrahedral hybrid orbitals. Deviations from perfect sp^3 hybridisation that occur are in a direction that concentrates s character in the lone-pair orbitals. This effect normally becomes more pronounced as the number of unshared electron pairs about the heavy atom increases.^[26]

The K^+ -coordinated $[\text{PPh}_2]^-$ ion of **1c** shows a more acute C_i–P–C_i' angle [$107.1(1)^\circ$] than the free $[\text{PPh}_2]^-$ ion [$108.3(1)^\circ$], however, the actual difference of $1.2(1)^\circ$ is very small. One reason for this seeming violation of Bent's rule could be that the interaction of P(1) with the two potassium ions is merely electrostatic in nature and thus has no pronounced effect on the orbital composition of the phosphorus atom. In the case of the two BBr_3 adducts **4Br** and **5Br**,

Figure 4. Crystal packing diagram of compound **9^c**.

we find a significantly smaller C_i-P-C_i' angle for the methyl derivative [**4Br**: $110.8(2)^\circ$, **5Br**: $106.5(5)^\circ$]. Given the well-known positive inductive effect of the CH_3 substituent, this indicates a higher p character in the P–Ph bonds of **5Br** than in those of **4Br**. Within the series **6** $\rightarrow$ **7** $\rightarrow$ **8**, only small differences between the individual C_i-P-C_i' angles are observed, which, moreover, do not follow a systematic trend since the respective angle in the mixed compound **7** does

not interpolate that of the doubly protonated molecule **6** and the doubly methylated compound **8**. By far the most pronounced deviation of C_i-P-C_i' from the ideal tetrahedral angle is observed in the adduct $K(18\text{-crown-6})\text{-}[(BH_3)_2PPh_2]$ (**9^c**). In line with Bent's rule, the value of $100.2(1)^\circ$, as compared to $107.6(2)^\circ$ in $[(CH_3)_2PPh_2]I$ (**8**), points towards a high degree of p character in the P– C_i bond orbitals of **9^c**. This interpretation is supported by the fact that the corresponding P– C_i bond lengths are significantly elongated [cf. **9^c**: $1.829(2)$ Å/ $1.831(2)$ Å; **8**: $1.794(3)$ Å]. In contrast to a priori expectations, they are even longer and the C_i-P-C_i' angle is more acute than in the potassium phosphide **1** [$1.807(2)$ Å to $1.817(2)$ Å; average value for C_i-P-C_i' : 107.7°].

NMR Spectroscopy: The most characteristic NMR parameters of the compounds **1–9** are compiled in Table 2.

For comparability and solubility reasons, all NMR spectra were run at ambient temperature (300 K). However, as $[H_2PPh_2]I$ (**6**) appeared to be largely dissociated in $CDCl_3$ solution under these conditions, the compounds **6** and **7** have also been investigated at low temperature (233 K) in order to shift the dissociation–association equilibrium to the adduct side (low-temperature data included in Table 2). In order to assess the relative degree of s and p character in the P–E bonding orbitals (E = H, C, B), we will mainly rely on the corresponding $^1J_{PE}$ coupling constants. Common wisdom has it that NMR coupling constants via a certain bond are governed by the Fermi contact term, which increases with increasing s character of the respective bond. We are aware of the fact that $^1J_{PE}$ values may change their sign upon going from one compound to another. In such cases, a correlation of $^1J_{PE}$ with the s character of the P–E bond is not possible until the signs of the coupling constants are known. We have not determined any relative sign data, however, it is firmly established in the literature that $^1J_{PB}$ coupling constants in phosphane–boranes^[27] as well as $^1J_{PH}$ coupling constants^[28] are generally positive. $^1J_{PC}$ coupling constants tend to be negative in three-coordinate phosphanes (cf. PPh_3 : $^1J_{PC} = -12.5$ Hz) and positive in compounds containing four-coordinate phosphorus centres (cf. $[PPh_4]^+$: $^1J_{PC} = +88.4$ Hz).^[28] For a detailed description

Table 2. Selected NMR parameters of compounds **1–9**; solvents: THF (**1–5Br**, **9**), $CDCl_3$ (**6–8**); upfield shifts are denoted by a minus sign and downfield shifts by a plus sign.

	Nucleus	Chemical shift values [ppm] ($^1J_{PX}$ [Hz])				
		^{31}P	^{11}B ($^1J_{PB}$)	$P-H$ ($^1J_{PH}$)	$P-^{13}C_i$ ($^1J_{PC}$)	$P-^{13}CH_3$ ($^1J_{PC}$)
1	$K[PPh_2]$	–9.8	–	–	157.1 (56.0)	–
2	$HPPH_2$	–39.5	–	5.11 (215.7)	135.4 (10.7)	–
3	CH_3PPh_2	–26.1	–	–	140.8 (10.0)	12.9 (12.0)
4H	$BH_3(H)PPh_2$	1.7	–40.0 (42)	6.16 (380.8)	127.6 (56.2)	–
4Br	$BBr_3(H)PPh_2$	–13.6	–17.1 (142)	6.97 (444.4)	121.3 (65.7)	–
5H	$BH_3(CH_3)PPh_2$	11.5	–37.9 (55)	–	131.9 (54.8)	11.4 (40.0)
5Br	$BBr_3(CH_3)PPh_2$	–9.2	–14.6 (150)	–	124.2 (68.2)	7.1 (48.7)
6	$[H_2PPh_2]I$	–31.0 ^[a]	–	9.91 (530.6) ^[a]	128.0 (83.0) ^[a]	–
7	$[CH_3(H)PPh_2]I$	–5.2 ^[a]	–	9.87 (521.7) ^[a]	115.9 (85.4) ^[a]	7.1 (53.8) ^[a]
8	$[(CH_3)_2PPh_2]I$	21.9	–	–	120.5 (87.6)	11.4 (56.4)
9	$K[(BH_3)_2PPh_2]$	–11.1	–34.6 (64)	–	140.2 (38.5)	–

[a] Recorded at 233 K.

of the effect of electron lone pairs on nuclear spin–spin coupling constants, the reader is referred to the work of Gil and Philipsborn.^[29]

At first, we are considering systematic changes in the NMR parameters of the three Lewis bases HPPH_2 (**2**), CH_3PPh_2 (**3**), and $[\text{BH}_3\text{PPh}_2]^-$ upon variation of the coordinated acid. Drake et al. have determined the P–H proton chemical shifts for five series of $\text{BX}_3\text{--P(H)RR'}$ adducts ($\text{R/R' = H/H, CD}_3\text{/H, CD}_3\text{/CD}_3$, Ph/H, Ph/Ph ; X = F, Cl, Br, I).^[14] As a general trend within any of the five groups, the shielding of the proton on phosphorus was found to decrease in a manner parallel to the accepted order of Lewis acidity ($\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$). Consistently, we observe a downfield shift of the P–H resonance along the series P(H)Ph_2 (**2**; $\delta = 5.11$) $\rightarrow$ $\text{BH}_3\text{--P(H)Ph}_2$ (**4H**; $\delta = 6.16$) $\rightarrow$ $\text{BBr}_3\text{--P(H)Ph}_2$ (**4Br**; $\delta = 6.97$) $\rightarrow$ $[\text{CH}_3\text{--P(H)Ph}_2]^+$ (**7**; $\delta = 9.87$) $\rightarrow$ $[\text{H--P(H)Ph}_2]^+$ (**6**; $\delta = 9.91$). Parallel to that, $^1J_{\text{PH}}$ becomes larger, thereby indicating an increasing degree of s character in the P–H bond. Moreover, the absolute value of the coupling constant $^1J_{\text{PCi}}$ between phosphorus and the *ipso* carbon atoms of the attached phenyl rings also increases in the same order: **2** (10.7 Hz) $<$ **4H** (56.2 Hz) $<$ **4Br** (65.7 Hz) $<$ **7** (85.4 Hz) $\approx$ **6** (83.0 Hz). A similar trend in the $^1J_{\text{PC}}$ values of the P–CH₃ and the P–Ph fragments is evident within the series of methylphosphane adducts: **3** $<$ **5H** $<$ **5Br** $<$ **7** $<$ **8** (Table 2). Thus, there is obviously an increase in s character in the P–H and P–C bonding orbitals of **2** and **3** upon adduct formation. Concomitantly, an increase in the p character of the phosphorus lone pair has to be postulated as it becomes involved in dative bonding. In line with the isovalent hybridisation hypothesis,^[26] the p character of the donor–acceptor bond is more pronounced when more Lewis acidic electrophiles are coordinated. Of special interest is an evaluation of the characteristic NMR parameters of the isoelectronic donors $\text{P(CH}_3)_2\text{Ph}_2$ (**3**) and $[\text{P(BH}_3)_2\text{Ph}_2]^-$ after coordination of $[\text{BH}_3]$, H^+ , and $[\text{CH}_3]^+$, respectively. As far as the ^{31}P – $^{13}\text{C}_i$ coupling constants are concerned, we obtain qualitatively similar results for both ligands with $^1J_{\text{PCi}}$ being consistently smaller in the $[\text{BH}_3]$ adducts as compared to the protonated or methylated derivatives {cf. $\text{K[BH}_3\text{--P(BH}_3)_2\text{Ph}_2]$ (**9**), $\text{H--P(BH}_3)_2\text{Ph}_2$ (**4H**), $\text{CH}_3\text{--P(BH}_3)_2\text{Ph}_2$ (**5H**): $^1J_{\text{PCi}} = 38.5$ Hz, 56.2 Hz, 54.8 Hz; $\text{BH}_3\text{--P(CH}_3)_2\text{Ph}_2$ (**5H**), $[\text{H--P(CH}_3)_2\text{Ph}_2]\text{I}$ (**7**), $[\text{CH}_3\text{--P(CH}_3)_2\text{Ph}_2]\text{I}$ (**8**): $^1J_{\text{PCi}} = 54.8$ Hz, 85.4 Hz, 87.6 Hz}.

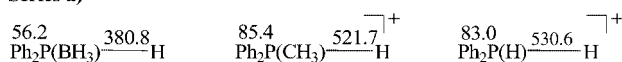
The ^{31}P NMR resonances within the series P(H)Ph_2 (**2**), $\text{BH}_3\text{--P(H)Ph}_2$ (**4H**), $\text{BBr}_3\text{--P(H)Ph}_2$ (**4Br**), and $[\text{CH}_3\text{--P(H)Ph}_2]\text{I}$ (**7**) possess chemical shift values of $\delta = -39.5$ ppm, 1.7 ppm, -13.6 ppm, and -5.2 ppm, respectively (Table 2). This observation is in agreement with the known fact that in most cases quaternisation of phosphanes leads to a downfield shift of the ^{31}P NMR signal as the shielding effect of the lone pair is removed.^[13] Deshielding is most pronounced after coordination of the isoelectronic and isosteric Lewis acids $[\text{BH}_3]$ and $[\text{CH}_3]^+$. Adduct formation of P(H)Ph_2 with BBr_3 leads to a smaller downfield shift. Within the series of $\text{P(CH}_3)_2\text{Ph}_2$ adducts, the following ^{31}P NMR shifts are observed (Table 2): **3** ($\delta = -26.1$), **5H** ($\delta = 11.5$), **5Br** ($\delta = -9.2$), **8** ($\delta = 21.9$). Thus, substitution of P–

CH_3 for P–H results in a general deshielding of the respective ^{31}P nucleus. The isosteric couples **4H/7**, **5H/8**, and **8/9** deserve special attention. The ^{31}P NMR resonance of $\text{H--P(BH}_3)_2\text{Ph}_2$ (**4H**) is shifted by 6.9 ppm to lower field as compared to the resonance of $[\text{H--P(CH}_3)_2\text{Ph}_2]\text{I}$ (**7**). However, this order is reversed and the absolute difference increases ($\Delta\delta = -10.4$) in the case of $\text{CH}_3\text{--P(BH}_3)_2\text{Ph}_2$ (**5H**; $\delta = 11.5$) vs. $[\text{CH}_3\text{--P(CH}_3)_2\text{Ph}_2]\text{I}$ (**8**; $\delta = 21.9$). Finally, the largest shift difference ($\Delta\delta = -33.0$) is found between $\text{K[BH}_3\text{--P(BH}_3)_2\text{Ph}_2]$ (**9**; $\delta = -11.1$) and $[\text{CH}_3\text{--P(CH}_3)_2\text{Ph}_2]\text{I}$ (**8**; $\delta = 21.9$).

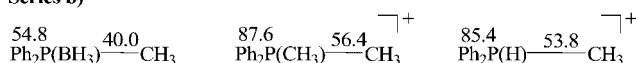
^{11}B NMR spectroscopy reveals a slight downfield shift of the boron nucleus upon going from **4H** ($\delta = -40.0$) to **5H** ($\delta = -37.9$) and **9** ($\delta = -34.6$). A qualitatively similar effect is observed for the couple **4Br/5Br** (Table 2).

In the second stage, we will now consider three groups of aggregates of the ligands P(H)Ph_2 (**2**), $\text{P(CH}_3)_2\text{Ph}_2$ (**3**), and $[\text{P(BH}_3)_2\text{Ph}_2]^-$ in which the Lewis acid is kept constant (Figure 5). Special emphasis is placed on the $^1J_{\text{DA}}$ coupling constants (D and A = donor and acceptor nuclei, respectively) because they are a property of the donor–acceptor bond in question and thus likely to provide insight into the relative base strengths of the three phosphorus donors. The proton adducts (series a, Figure 5) show similar $^1J_{\text{PH}}$ values for the P(H)Ph_2 and $\text{P(CH}_3)_2\text{Ph}_2$ ligand and a much smaller value in $\text{H--P(BH}_3)_2\text{Ph}_2$. The same is true for $^1J_{\text{PC}}$ in the $[\text{CH}_3]^+$ adducts of series b (Figure 5).

Series a)



Series b)



Series c)

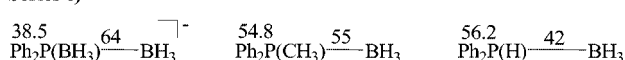


Figure 5. Systematic trends in the $^1J_{\text{DA}}$ and $^1J_{\text{PCi}}$ coupling constants along three series of $[\text{P(BH}_3)_2\text{Ph}_2]^-$, $\text{P(CH}_3)_2\text{Ph}_2$, and P(H)Ph_2 adducts.

Thus, compared to the neutral phosphane ligands, $[\text{P(BH}_3)_2\text{Ph}_2]^-$ is able to provide an electron pair of higher p character such that the charge density is more strongly polarized in the direction of the acceptor orbital. This interpretation most likely holds also for the $[\text{BH}_3]$ adducts of series c (Figure 5) even though ^{31}P – ^{11}B coupling via the dative bond is now *larger* in $\text{K[BH}_3\text{--P(BH}_3)_2\text{Ph}_2]$ (**9**) and *smaller* in $\text{BH}_3\text{--P(H)Ph}_2$ (**4H**), and $\text{BH}_3\text{--P(CH}_3)_2\text{Ph}_2$ (**5H**). Here, the decisive factor is the rehybridisation of $[\text{BH}_3]$ as it moves from a planar sp^2 configuration to a tetrahedral sp^3 arrangement. As a consequence, we are facing two opposing trends:^[14] When phosphane forms an adduct, the phosphorus orbital involved in bond formation decreases in s character. On the other hand, the stronger the donor–acceptor interaction, the more pyramidalized the coordinated borane which in turn results in more B(2s) character being diverted into the P–B bond. Despite of the fact that

a quantitative assessment of these two competing factors is obviously difficult, an empirical correlation between the magnitude of $^1J_{\text{PB}}$ and dative bond strength became evident from several studies on $[\text{BH}_3]$ adducts of selected series employing smoothly varying phosphane ligands.^[14,30–32] Based on the development of $^1J_{\text{PB}}$ coupling constants along the sequence **4H** (42 Hz), **5H** (55 Hz), and **9** (64 Hz) we therefore confidently assign the highest Lewis basicity to the phosphanylborohydride ligand $[\text{P}(\text{BH}_3)\text{Ph}_2]^-$ (note that for $\text{Li}[(\text{BH}_3)_2\text{P}(\text{CH}_3)_2]$ a coupling constant $^1J_{\text{PB}} = 107$ Hz has been published,^[33] which is even larger than $^1J_{\text{PB}}$ of **9**).

To test this hypothesis, two displacement experiments have been carried out and monitored by ^{31}P NMR spectroscopy. First, we investigated an equimolar mixture of $\text{K}[(\text{BH}_3)_2\text{PPh}_2]$ (**9**) and CH_3PPh_2 (**3**) in THF. Even after prolonged storage of the NMR vessel at ambient temperature, no transfer of $[\text{BH}_3]$ with formation of $\text{K}[\text{BH}_3\text{PPh}_2]$ and $\text{BH}_3(\text{CH}_3)\text{PPh}_2$ (**5H**) was observable. The result remained the same at higher temperatures. In contrast, between $\text{BH}_3(\text{CH}_3)\text{PPh}_2$ (**5H**) and $\text{K}[\text{BH}_3\text{PPh}_2]$ a reaction to CH_3PPh_2 (**3**) and $\text{K}[(\text{BH}_3)_2\text{PPh}_2]$ (**9**) takes place already at ambient temperature (ca. 10% conversion after 2 d). Heating of the sample to a temperature of 50 °C for 2 h leads to ca. 50% conversion.

Conclusion

Based on NMR spectroscopy ($^1J_{\text{PB}}$ values) and displacement experiments we come to the conclusion that the phosphanylborohydride ligand $[\text{BH}_3\text{PPh}_2]^-$ possesses a higher Lewis basicity towards $[\text{BH}_3]$ than its neutral isoelectronic and isostructural congener $\text{P}(\text{CH}_3)\text{Ph}_2$. Moreover, NMR spectroscopy ($^1J_{\text{PB}}$, $^1J_{\text{PH}}$, and $^1J_{\text{PCi}}$ values) and X-ray crystallography ($\text{C}_i\text{--P--C}_i'$ angles; $\text{C}_i = ipso$ carbon atom of the phenyl ring) on selected adducts of the ligands HPPH_2 , CH_3PPh_2 , and $[\text{BH}_3\text{PPh}_2]^-$ indicate $[\text{BH}_3\text{PPh}_2]^-$ to form dative bonds of the highest p character within this series. Consequently, $[\text{BH}_3\text{PPh}_2]^-$ is best suited to direct the charge density of its electron lone pair in the direction of the acceptor orbital of a coordinated Lewis acid.

Experimental Section

General Considerations: All reactions and manipulations of air-sensitive compounds were carried out under dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/benzophenone (THF, diethyl ether, toluene) or sodium-lead alloy (pentane, hexane) prior to use. NMR spectra were recorded with Bruker AMX 250 or AMX 400 spectrometers. Approximately 0.1 mL of C_6D_6 was added to all samples recorded in undeuterated THF (0.6 mL) to provide a lock signal. ^1H - and ^{13}C NMR shifts are reported relative to tetramethylsilane and were referenced against residual solvent peaks ($\text{C}_6\text{D}_5\text{H}$: $\delta = 7.16$, C_6D_6 : $\delta = 128.06$; CHCl_3 : $\delta = 7.26$, CDCl_3 : $\delta = 77.16$ ppm).^[34] ^{11}B NMR spectra were referenced against external $\text{BF}_3\cdot\text{OEt}_2$. ^{31}P NMR spectra are reported relative to external H_3PO_4 (85%). Abbreviations: s = singlet, d = doublet, tr = triplet, vtr = virtual triplet, q = quartet, dq = doublet of quartets, m = multiplet, br. = broad, n.o. =

signal not observed, *i* = ipso, *o* = ortho, *m* = meta, *p* = para. Elemental analyses were performed by the microanalytical laboratory of the J. W. Goethe University, Frankfurt/Main, Germany.

Materials: Lithium and potassium metal, PPh_3 , CH_3PPh_2 (**3**), $\text{BH}_3\cdot\text{THF}$ solution (1 mol/L in THF) and 18-crown-6 were purchased from Aldrich or Fluka and used as received. HPPH_2 (**2**) was obtained through reductive cleavage of triphenylphosphane with lithium powder in THF and subsequent hydrolysis and distillation as described by Bianco and Doronzo.^[35]

Synthesis of $\text{K}[\text{PPh}_2]$ (1**):** The compound was obtained through deprotonation of HPPH_2 (**2**; 320 mg, 1.72 mmol) with potassium metal (120 mg, 3.07 mmol) in THF (5 mL). The resulting orange solution was decanted from excess potassium and directly used for the NMR measurements. X-ray quality crystals of **1**·18-crown-6 (**1'**) were grown by gas-phase diffusion of diethyl ether into a THF solution containing $\text{K}[\text{PPh}_2]$ and an equimolar amount of 18-crown-6. ^1H NMR (THF, 250.13 MHz): $\delta = 6.42$ (tr, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, H-*p*), 6.73 (vtr, $^3J_{\text{HH}} = 7.5$ Hz, 4 H, H-*m*) 7.40–7.49 (m, 4 H, H-*o*) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF, 62.90 MHz): $\delta = 118.6$ (br., C-*p*), 127.5 (d, $^3J_{\text{PC}} = 5.5$ Hz, C-*m*), 129.2 (d, $^2J_{\text{PC}} = 18.6$ Hz, C-*o*), 157.1 (br. d, $^1J_{\text{PC}} = 56.0$ Hz, C-*i*) ppm. ^{31}P NMR (THF, 161.98 MHz): $\delta = -9.8$ (s) ppm.

Synthesis of $\text{BH}_3(\text{H})\text{PPh}_2$ (4H**):** To a solution of HPPH_2 (2.53 g, 13.5 mmol) in THF (10 mL) was added a calibrated solution (1 mol/L) of $\text{BH}_3\cdot\text{THF}$ in THF (13.5 mL, 13.5 mmol) at -78 °C with stirring. After the mixture had been warmed to ambient temperature overnight, all volatiles were removed in vacuo. The resulting oily residue was purified by column-chromatography (50 g silica-gel; eluent: hexane/toluene, 1:1). After evaporation of the eluate, the resulting oil of **4H** was triturated with pentane whereupon it solidified to give a colourless waxy material. Yield: 2.29 g (85%). ^1H NMR (THF, 400.13 MHz): $\delta = 1.15$ (q, $^1J_{\text{BH}} = 100$ Hz, 3 H, BH_3), 6.16 (dq, $^1J_{\text{PH}} = 380.8$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, 1 H, PH), 7.19–7.30 (m, 6 H, H-*m,p*), 7.51–7.65 (m, 4 H, H-*o*) ppm. ^{11}B NMR (THF, 128.38 MHz): $\delta = -40.0$ (dq, $^1J_{\text{PB}} = 42$ Hz, $^1J_{\text{BH}} = 100$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF, 62.90 MHz): $\delta = 127.6$ (d, $^1J_{\text{PC}} = 56.2$ Hz, C-*i*), 129.3 (d, $^3J_{\text{PC}} = 10.1$ Hz, C-*m*), 131.8 (d, $^4J_{\text{PC}} = 2.5$ Hz, C-*p*) 133.3 (d, $^2J_{\text{PC}} = 9.3$ Hz, C-*o*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, 161.98 MHz): $\delta = 1.7$ (m) ppm.

Synthesis of $\text{BBr}_3(\text{H})\text{PPh}_2$ (4Br**):** The compound was synthesised from BBr_3 (320 mg, 1.28 mmol) and HPPH_2 (230 mg, 1.24 mmol) in hexane (5 mL) as described in the literature.^[14] Yield: 489 mg (92%). X-ray-quality crystals were grown by gas-phase diffusion of pentane into a solution of **4Br** in toluene. Since the compound is not stable in THF for extended periods of time, NMR measurements have to be carried out immediately after sample preparation. $\text{C}_{12}\text{H}_{11}\text{BBr}_3\text{P}$ (436.72): calcd. C 33.00, H 2.54; found: C 33.15, H 2.50. ^1H NMR (THF, 400.13 MHz): $\delta = 6.97$ (d, $^1J_{\text{PH}} = 444.4$ Hz, 1 H, PH), 7.31–7.39 (m, 4 H, H-*m*), 7.43–7.48 (m, 2 H, H-*p*), 7.76–7.84 (m, 4 H, H-*o*) ppm. ^{11}B NMR (THF, 128.38 MHz): $\delta = -17.1$ (d, $^1J_{\text{PB}} = 142$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF, 100.62 MHz): $\delta = 121.3$ (d, $^1J_{\text{PC}} = 65.7$ Hz, C-*i*), 129.7 (d, $^3J_{\text{PC}} = 11.7$ Hz, C-*m*), 133.4 (d, $^4J_{\text{PC}} = 2.8$ Hz, C-*p*), 134.6 (d, $^2J_{\text{PC}} = 8.2$ Hz, C-*o*) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF, 161.98 MHz): $\delta = -13.6$ (q, $^1J_{\text{PB}} = 142$ Hz) ppm.

Synthesis of $\text{BH}_3(\text{CH}_3)\text{PPh}_2$ (5H**):** To a solution of CH_3PPh_2 (270 mg, 1.35 mmol) in THF (2 mL) was added a calibrated solution (1 mol/L) of $\text{BH}_3\cdot\text{THF}$ in THF (1.3 mL, 1.3 mmol) at -78 °C with stirring. After the mixture had been warmed to ambient temperature overnight, all volatiles were removed in vacuo. **5H** was obtained in essentially quantitative yield as a colourless oil. ^1H NMR (THF, 250.13 MHz): $\delta = 1.03$ (q, 3 H, BH_3), 1.66 (d, $^2J_{\text{PH}}$

= 10.0 Hz, 3 H, CH₃), 7.18–7.31 (m, 6 H, H-*m,p*), 7.51–7.63 (m, 4 H, H-*o*) ppm. ¹¹B NMR (THF, 128.38 MHz): δ = −37.9 (dq, ¹J_{PB} = 55 Hz, ¹J_{BH} = 99 Hz) ppm. ¹³C{¹H} NMR (THF, 62.90 MHz): δ = 11.4 (d, ¹J_{PC} = 40.0 Hz, CH₃), 129.0 (d, ³J_{PC} = 9.8 Hz, C-*m*), 131.2 (d, ⁴J_{PC} = 2.4 Hz, C-*p*), 131.9 (d, ¹J_{PC} = 54.8 Hz, C-*i*), 132.2 (d, ²J_{PC} = 9.6 Hz, C-*o*) ppm. ³¹P{¹H} NMR (THF, 161.98 MHz): δ = 11.5 (m) ppm.

Synthesis of BBr₃(CH₃)PPh₂ (5Br): The compound was synthesised from CH₃PPh₂ (235 mg, 1.17 mmol) and BBr₃ (302 mg, 1.21 mmol) in hexane (5 mL) following a published procedure.^[16] Yield: 487 mg

(90%). X-ray quality crystals were grown by gas-phase diffusion of pentane into a solution of **5Br** in toluene. C₁₃H₁₃BBr₃P (450.74): calcd. C 34.64, H 2.91; found: C 34.41, H 2.79. ¹H NMR (THF, 400.13 MHz): δ = 2.11 (d, ²J_{PH} = 11.9 Hz, 3 H, CH₃), 7.28–7.34 (m, 4 H, H-*m*), 7.39–7.44 (m, 2 H, H-*p*), 7.74–7.80 (m, 4 H, H-*o*) ppm. ¹¹B NMR (THF, 128.38 MHz): δ = −14.6 (d, ¹J_{PB} = 150 Hz) ppm. ¹³C{¹H} NMR (THF, 100.62 MHz): δ = 7.1 (d, ¹J_{PC} = 48.7 Hz, CH₃), 124.2 (d, ¹J_{PC} = 68.2 Hz, C-*i*), 129.2 (d, ³J_{PC} = 10.9 Hz, C-*m*), 132.9 (d, ⁴J_{PC} = 2.7 Hz, C-*p*), 134.3 (d, ²J_{PC} = 8.1 Hz, C-*o*) ppm. ³¹P{¹H} NMR (THF, 161.98 MHz): δ = −9.2 (q, ¹J_{PB} = 150 Hz) ppm.

Table 3. Crystallographic data for compounds **1^c**, **4Br**, **5Br**, **6**, **7**, and **9^c**.

	1^c	4Br	5Br
Formula	C ₂₄ H ₃₄ KO ₆ P	C ₁₂ H ₁₁ BBr ₃ P	C ₁₃ H ₁₃ BBr ₃ P
<i>F</i> _w	488.58	436.72	450.74
Colour, shape	orange, block	colourless, plate	colourless, block
Temperature [K]	173(2)	173(2)	173(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	10.5151(7)	10.2401(3)	32.935(5)
<i>b</i> [Å]	14.8018(7)	8.7189(3)	7.074(1)
<i>c</i> [Å]	32.593(2)	32.686(2)	13.842(2)
<i>a</i> [°]	90	90	90
<i>β</i> [°]	96.286(5)	90	100.25(1)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	5042.4(5)	2918.3(2)	3173.4(8)
<i>Z</i>	8	8	8
<i>D</i> _{calcd.} [g cm ^{−3}]	1.287	1.988	1.887
<i>F</i> (000)	2080	1664	1728
<i>μ</i> [mm ^{−1}]	0.310	8.378	7.708
Crystal size [mm]	0.49 × 0.46 × 0.42	0.28 × 0.26 × 0.13	0.28 × 0.26 × 0.24
Reflections collected	20677	46394	8766
Independent reflections (<i>R</i> _{int})	9044 (0.0392)	3151 (0.0887)	2800 (0.1247)
Data/restraints/parameters	9044/0/577	3151/0/159	2800/0/163
GOOF on <i>F</i> ²	0.981	1.077	1.102
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0423, 0.1043	0.0391, 0.1046	0.0839, 0.2000
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0599, 0.1122	0.0419, 0.1073	0.0981, 0.2116
Largest diff. peak and hole [e·Å ^{−3}]	0.688 and −0.404	0.951 and −0.643	1.345 and −2.047
	6	7	9^c
Formula	C ₁₂ H ₁₂ IP	C ₁₃ H ₁₄ IP	C ₂₄ H ₄₀ B ₂ KO ₆ P
<i>F</i> _w	314.09	328.11	516.25
Colour, shape	colourless, block	colourless, block	colourless, block
Temperature [K]	173(2)	173(2)	173(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	8.8460(5)	16.2294(7)	8.4076(10)
<i>b</i> [Å]	14.3281(9)	9.6942(3)	19.714(2)
<i>c</i> [Å]	9.8352(6)	17.1034(6)	16.867(2)
<i>a</i> [°]	90	90	90
<i>β</i> [°]	99.437(5)	90	96.674(10)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	1229.7(1)	2690.9(2)	2776.7(6)
<i>Z</i>	4	8	4
<i>D</i> _{calcd.} [g cm ^{−3}]	1.697	1.620	1.235
<i>F</i> (000)	608	1280	1104
<i>μ</i> [mm ^{−1}]	2.695	2.467	0.284
Crystal size [mm]	0.37 × 0.33 × 0.25	0.27 × 0.25 × 0.24	0.48 × 0.46 × 0.43
Reflections collected	19524	57301	11881
Independent reflections (<i>R</i> _{int})	2229 (0.0363)	3902 (0.0384)	5347 (0.0739)
Data/restraints/parameters	2229/0/136	3902/0/141	5347/0/309
GOOF on <i>F</i> ²	1.087	1.298	0.871
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0161, 0.0389	0.0297, 0.0706	0.0404, 0.0950
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0175, 0.0395	0.0312, 0.0724	0.0549, 0.0982
Largest diff. peak and hole [e·Å ^{−3}]	0.289 and −0.439	0.493 and −0.560	0.611 and −0.460

Synthesis of [H₂PPh₂]I** (**6**):** For the synthesis of **6**, HPPH₂ (322 mg, 1.73 mmol) was treated with excess HI in toluene (3 mL) at –78 °C. Yield: 429 mg (80%). Crystals suitable for X-ray crystallography formed when a concentrated CHCl₃ solution of **6** was slowly cooled to –30 °C. C₁₂H₁₂IP (314.09): calcd. C 45.89, H 3.85; found: C 46.16, H 3.83. ¹H NMR (CDCl₃, 250.13 MHz, 300 K): δ = 5.8 (very br., 2 H, PH₂), 7.41–7.56 (m, 6 H, H-*m,p*), 7.73–7.84 (m, 4 H, H-*o*) ppm. ¹H NMR (CDCl₃, 250.13 MHz, 233 K): δ = 7.45–7.85 (m, 6 H, H-*m,p*), 7.94–8.15 (m, 4 H, H-*o*), 9.91 (br. d, 2 H, PH₂) ppm. ¹³C{¹H} NMR (CDCl₃, 62.90 MHz, 300 K): broad, poorly resolved signals. ¹³C{¹H} NMR (CDCl₃, 62.90 MHz, 233 K): 128.0 (d, ¹J_{PC} = 83.0 Hz, C-*i*), 129.2 (d, ³J_{PC} = 13.2 Hz, C-*m*), 131.1 (d, ²J_{PC} = 11.8 Hz, C-*o*), 133.4 (d, ⁴J_{PC} = 1.6 Hz C-*p*) ppm. ³¹P{¹H} NMR (CDCl₃, 161.98 MHz, 300 K): δ = –34.2 (br. s) ppm. ³¹P{¹H} NMR (CDCl₃, 161.98 MHz, 233 K): δ = –31.0 (tr, ¹J_{PH} = 530.6 Hz) ppm.

Synthesis of [CH₃(H)PPh₂]I** (**7**):** Following a published procedure,^[17] CH₃PPh₂ (336 mg, 1.68 mmol) was treated with excess HI in toluene (3 mL) at –78 °C. Yield: 385 mg (70%). Crystals suitable for X-ray crystallography formed when a concentrated CHCl₃ solution of **7** was slowly cooled to –30 °C. C₁₃H₁₄IP (328.11): calcd. C 47.59, H 4.30; found: C 47.82, H 4.53. ¹H NMR (CDCl₃, 250.13 MHz, 300 K): δ = 2.58 (d, ²J_{PH} = 14.7 Hz, 3 H, CH₃), 7.51–7.61 (m, 4 H, H-*m*), 7.64–7.73 (m, 2 H, H-*p*), 7.91–8.03 (m, 4 H, H-*o*), 10.1 (d, ¹J_{PH} = 521.7 Hz, 1 H, PH) ppm. ¹H NMR (CDCl₃, 250.13 MHz, 233 K): δ = 2.57 (dd, ²J_{PH} = 14.6 Hz, ³J_{HH} = 5.7 Hz, 3 H, CH₃), 7.47–8.01 (m, 10 H, H-*o/m/p*), 9.87 (d, ¹J_{PH} = 521.7 Hz, 1 H, PH) ppm. ¹³C{¹H} NMR (CDCl₃, 62.90 MHz, 300 K): δ = 7.7 (d, ¹J_{PC} = 54.1 Hz, CH₃), 116.8 (d, ¹J_{PC} = 84.9 Hz, C-*i*), 130.3 (d, ³J_{PC} = 13.2 Hz, C-*m*), 133.3 (d, ²J_{PC} = 10.9 Hz, C-*o*), 135.1 (d, ⁴J_{PC} = 3.1 Hz, C-*p*) ppm. ¹³C{¹H} NMR (CDCl₃, 62.90 MHz, 233 K): δ = 7.1 (d, ¹J_{PC} = 53.8 Hz, CH₃), 115.9 (d, ¹J_{PC} = 85.4 Hz, C-*i*), 130.2 (d, ³J_{PC} = 13.1 Hz, C-*m*), 133.0 (d, ²J_{PC} = 10.8 Hz, C-*o*), 135.1 (br., C-*p*) ppm. ³¹P{¹H} NMR (CDCl₃, 161.98 MHz, 300 K): δ = –4.7 (s) ppm. ³¹P{¹H} NMR (CDCl₃, 161.98 MHz, 233 K): δ = –5.2 (s) ppm.

Synthesis of [(CH₃)₂PPh₂]I** (**8**):** The compound was synthesised following a published procedure^[36] via the reaction of HPPH₂ (204 mg, 1.10 mmol) with ICH₃ (217 mg, 1.53 mmol) in THF (4 mL). Yield: 353 mg (94%). Crystals suitable for X-ray crystallography formed when a concentrated CHCl₃ solution of **8** was slowly cooled to –30 °C. C₁₄H₁₆IP (342.15): calcd. C 49.15, H 4.71; found: C 48.92, H 4.58. ¹H NMR (CDCl₃, 250.13 MHz): δ = 2.88 (d, ²J_{PH} = 13.9 Hz, 3 H, CH₃), 7.60–7.79 (m, 6 H, H-*m,p*), 7.83–7.95 (m, 4 H, H-*o*) ppm. ¹³C{¹H} NMR (CDCl₃, 62.90 MHz): δ = 11.4 (d, ¹J_{PC} = 56.4 Hz, CH₃), 120.5 (d, ¹J_{PC} = 87.6 Hz, C-*i*), 130.3 (d, ³J_{PC} = 12.8 Hz, C-*m*), 132.3 (d, ²J_{PC} = 10.7 Hz, C-*o*), 135.0 (d, ⁴J_{PC} = 3.0 Hz, C-*p*) ppm. ³¹P{¹H} NMR (CDCl₃, 161.98 MHz): δ = 21.9 (s) ppm.

Synthesis of K[(BH₃)₂PPh₂]I** (**9**):** To a solution of 435 mg K[BH₃PPh₂] (1.82 mmol) in THF (5 mL) was added a calibrated solution (1 mol/L) of BH₃·THF (1.8 mL, 1.8 mol) at –78 °C with stirring. After 30 min, the cooling bath was removed and the reaction mixture warmed to ambient temperature with subsequent stirring for another 60 min. All volatiles were removed in vacuo and the resulting colourless solid was washed twice with pentane (2 mL). Yield: 423 mg (92%). X-ray quality crystals were grown by gas-phase diffusion of diethyl ether onto a solution containing K[(BH₃)₂PPh₂] and an equimolar amount of 18-crown-6. C₂₄H₄₀B₂KO₆P (516.25): calcd. C 55.84, H 7.81; found C 55.38, H 7.63. ¹H NMR (THF, 250.13 MHz): δ = 1.0 (q, ¹J_{BH} = 89 Hz, 6 H, BH₃), 7.00–7.10 (m, 6 H, H-*m,p*), 7.74–7.85 (m, 4 H, H-*o*) ppm.

¹¹B{¹H} NMR (THF, 128.38 MHz): δ = –34.6 (d, ¹J_{PB} = 64 Hz, BH₃) ppm. ¹³C{¹H} NMR (THF, 62.90 MHz): 127.4 (d, ³J_{PC} = 8.2 Hz, C-*m*), 127.9 (d, ⁴J_{PC} = 2.0 Hz, C-*p*), 133.4 (d, ²J_{PC} = 7.7 Hz, C-*o*), 140.2 (d, ¹J_{PC} = 38.5 Hz, C-*i*) ppm. ³¹P NMR (THF, 161.98 MHz): δ = –11.1 (m) ppm.

X-ray Structural Characterisation: Data collections were performed on a Stoe IPDS-II two-circle diffractometer with graphite-monochromated Mo-*K*_α radiation. Empirical absorption corrections with the MULABS option^[37] in the program PLATON^[38] were performed. Equivalent reflections were averaged. The structures were solved by direct methods^[39] and refined with full-matrix least-squares on *I*² using the program SHELXL-97.^[40] Hydrogen atoms bonded to carbon and boron were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. H atoms bonded to phosphorus were refined isotropically. Details of the X-ray crystal structure analyses of **1**^c, **4Br**, **5Br**, **6**, **7**, and **9**^c are summarised in Table 3.

CCDC-290838 (for **1**^c), -290839 (for **4Br**), -290840 (for **5Br**), -290841 (for **6**), -290842 (for **7**), and -290843 (for **9**^c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (for details see the footnote on the first page of this article): ORTEP drawings of **4Br**, **5Br**, **6**, **7**, and **8**.

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