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A Comparative Study of Chalcogenated Phosphanylborohydrides $[EPR_2BH_3]^-$ (R = Ph, *t*Bu) and Triorganophosphane Chalcogenides $EPPh_2CH_3$ (E = O, S, Se, Te)

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Chalcogenation of the phosphanylborohydrides $K(PPh_2BH_3)$ and $K(PtBu_2BH_3)$ with N_2O, S_8, Se_∞, and Te_∞ leads to the corresponding species $K(EPR_2BH_3)$ in excellent yield (E = O–Te; R = Ph, *t*Bu). The parent systems as well as all the chalcogen derivatives have been structurally characterised as their 18-crown-6 adducts by X-ray crystallography. In the case of $[K(18\text{-c-}6)][EPPh_2BH_3]$ the anionic ligand binds to the K^+ ion through both its E atom and its BH_3 substituent. Significantly larger K–B distances together with shorter K–E contacts are observed in the sterically more congested *tert*-butyl derivatives $[K(18\text{-c-}6)][EPtBu_2BH_3]$. Based on a comparison of characteristic NMR parameters (e.g. $^1J_{P,B}$, $^1J_{P,C}$) of $K(EPPh_2BH_3)$ and $EPPh_2CH_3$, we come to the conclusion that the formal replacement of CH_3^+ by BH_3 leads to a significant increase in the p character of the E–P bond, which therefore indicates that $[PPh_2BH_3]^-$ is better suited to direct electron density towards an acceptor atom than its triorganophosphane congener PPh_2CH_3. In line with this interpretation, displacement experiments between $K(PPh_2BH_3)$ and $EPPh_2CH_3$ (E = S–Te) resulted in the quantitative formation of $K(EPPh_2BH_3)$ and PPh_2CH_3.

Introduction

Organophosphanes are among the most abundant ligands in coordination chemistry,[1] therefore much effort is still devoted to the design of improved phosphane ligand systems with customised steric and electronic properties. Of particular importance is a targeted tuning of the Lewis basicity of the phosphorus atom in triorganophosphanes (PR_3) by careful variation of the R substituents. For example, aryl substituents result in phosphanes of medium donor strength (cf. PPh_3), while more electron-releasing alkyl substituents lead to an increased σ-donor ability (cf. PEt_3).[2] Given this background, it is interesting to explore whether replacement of an alkyl side-chain by the even less electronegative BH_3 fragment further promotes the capability of the phosphorus centre to deliver charge density to a coordinated acceptor atom. So far, the chemistry of such phosphanylborohydrides $[PR_2BH_3]^-$ has not been systematically developed, although a number of publications already exist that clearly prove the potential of phosphanylborohydrides in areas as diverse as the synthesis of polymeric materials containing group 13 and group 15 elements,[3] the preparation of chiral organophosphanes,[4–7] general coordination chemistry,[8–10] and homogeneous catalysis.[11] Our group has recently reported an assessment of the relative Lewis basicities of $[PPh_2BH_3]^-$, PPh_2CH_3 and PPh_2H towards the Lewis acids H^+, $[CH_3]^+$ and BH_3.[12] In the corresponding adducts the ligands were treated as σ-donors and effects of π-backbonding, which, if present, are only relevant in the BH_3 adducts,[13] were neglected. The situation changes when triorganophosphane chalcogenides (EPR_3) and chalcogenated phosphanylborohydrides $[EPR_2BH_3]^-$ are included in the discussion. Especially in the case of phosphane oxides, the great stability of the OP group is most likely derived from multiple bonding. A nowadays widely accepted description of the multiple bond in the phosphoryl fragment suggests a donor–acceptor interaction between the electron lone-pair on phosphorus and the oxygen atom (σ-bond) superimposed by a transfer of electron density from two filled 2p orbitals on oxygen to a set of antibonding orbitals of e symmetry on the PR_3 fragment (π-bonds; *negative hyperconjugation*[14]).[15] Other theories, however, explain the short, strong and highly polar O–PR_3 bond by means of σ donation from P to O, which leads to a pronounced charge separation of the form $^-O\text{-}^+PR_3$ and, in turn, strengthens and shortens the O–P bond due to electrostatic attraction.[16,17]

The purpose of this paper is to compare the structural and NMR spectroscopic properties of compounds $[EPR_2BH_3]^-$ with those of related triorganylphosphane chalcogenides. Electronegative groups on phosphorus are known[18] to increase the degree of multiple bonding in OPR_3 compounds and it is therefore interesting to unveil

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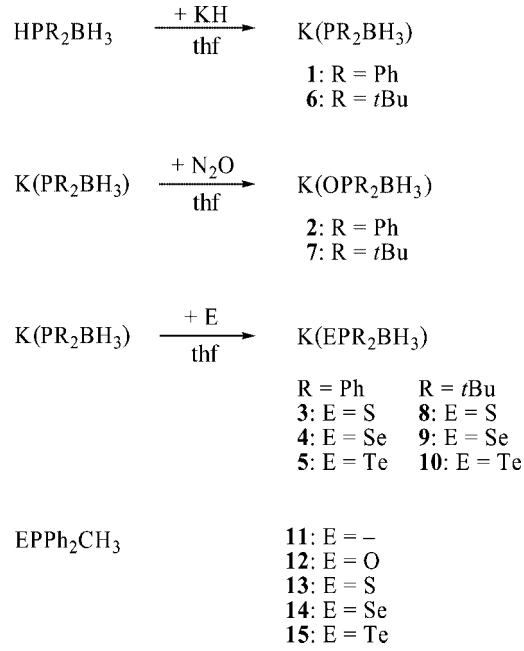
the influence of the electropositive BH_3 substituent on the electron distribution within the $[EPR_2BH_3]^-$ framework. Since it is well-known that a delicate interplay exists between steric and electronic effects in phosphane ligands,[2] we have chosen methylbis(phenyl)phosphane (PPh_2CH_3) and bis(phenyl)phosphanylborohydride $[PPh_2BH_3]^-$ for our comparative studies since these two compounds are largely isostructural. To elucidate the consequences of steric bulk on the ligand properties of phosphanylborohydrides the *tert*-butyl derivative $[PtBu_2BH_3]^-$ was also included in our investigation.

Results and Discussion

Syntheses

The phosphanylborohydrides $K(PR_2BH_3)$ [R = Ph (**1**), *t*Bu (**6**); Scheme 1] are readily accessible by deprotonation of the corresponding phosphane–borane adducts HPR_2BH_3 with potassium hydride in thf. Stirring of thf solutions of $K(PR_2BH_3)$ under an atmosphere of dry nitrous oxide leads to the clean formation of $K(OPR_2BH_3)$ (**2**, **7**). Complexes of the heavier chalcogens (**3**–**5** and **8**–**10**) were obtained upon treatment of $K(PR_2BH_3)$ with elemental sulfur, grey selenium or tellurium in thf (Scheme 1). In all cases, the yields were high. The molecules contain a P–B bond and there is no migration of BH_3 from the phosphorus to the chalcogen atom. Similar to this, secondary phosphane oxides also prefer $R_2(O)PH$ structures over the tautomeric forms R_2POH.[18] $R_2(O)PH$ compounds are weak acids and the proton on phosphorus can be removed with appropriate bases. In most transformations the resulting $[R_2(O)P:]^-$ intermediates react with electrophiles at the phosphorus site, thus preserving the phosphoryl group in the product. Consequently, our derivatives $K(OPR_2BH_3)$ (**2**, **7**) may be viewed as Lewis acid–base adducts between BH_3 and $K[R_2(O)P:]$. The O, S and Se derivatives **2**–**4** and **7**–**9** are reasonably stable towards air and moisture. Exposure of the Te derivatives **5** and **10** to water, however, instantaneously leads to the liberation of elemental tellurium together with the formation of HPR_2BH_3. The compounds also lose tellurium upon contact with silicone grease. It is interesting to note that **5**, even though it is not a very stable compound, can be synthesised, isolated and structurally characterised. This stands in marked contrast to the related triorganophosphane telluride $TePPh_2CH_3$, which forms only as minor component in a dynamic equilibrium when the phosphane PPh_2CH_3 is treated with tellurium in thf solution. Since this result already indicates phosphanylborohydrides $[PR_2BH_3]^-$ to be stronger Lewis bases than their triorganylphosphane counterparts, it prompted us to investigate whether a displacement reaction occurs between $K(PPh_2BH_3)$ (**1**) and the chalcogenides $EPPh_2CH_3$ (E = O, S, Se; **12**–**14**). Indeed, in situ ^{31}P NMR spectroscopy revealed quantitative transfer of the E atom from **13** and **14** to the phosphanylborohydride **1** in thf solution. In the case of **1**/**14**, the exchange of the selenium atom proceeds instantaneously at room temp., whereas sulfur transfer from **13** to **1** requires heating of the reaction mixture to 65 °C for 18 h. Under the same conditions an equimolar mixture of **1** and **12** remains unchanged. We believe that the reaction between **1** and **12**, even though thermodynamically favourable, is prevented by a high activation barrier.



Scheme 1. Synthesis of the potassium phosphanylborohydrides **1** and **6** and their chalcogenation to **2**–**5** and **7**–**10**, along with the numbering scheme of the related methylbis(phenyl)phosphane **11** and its chalcogenides **12**–**15**.

The IR stretching frequency of the EP bond is a useful characteristic of compounds $K(EPR_2BH_3)$ (R = Ph, *t*Bu). Unfortunately, it was not possible to unambiguously assign the band of the EP stretch in the fingerprint region of the IR spectrum of any of the molecules under investigation here.

X-ray Crystallography

X-ray quality crystals of the 18-crown-6 adducts **1**^{c}–**5**^{c} were obtained by gas-phase diffusion of diethyl ether onto solutions containing **1**–**5** and equimolar amounts of 18-crown-6. Single-crystals of the adducts **6**^{c}–**10**^{c} were grown by cooling their concentrated solutions in diethyl ether to –30 °C. Neutral methylbis(phenyl)phosphane oxide (**12**) was crystallised by allowing its hot, saturated, hexane solution to cool to room temp. Crystallographic data for compounds **1**^{c}–**10**^{c} and **12** are given in the Experimental Section; selected bond lengths and angles are compiled in Table 1.

Each K^+ ion in **1**^{c}–**10**^{c} is bonded to the six oxygen atoms of one 18-crown-6 ligand and to one chalcogenophosphorylic anion. In most cases, short K···B distances indicate K^+ coordination of the BH_3 substituent in addition to K–E adduct formation (Table 1; E = O, S, Se, Te). According to Edelstein's correlation[19] of metal···boron distances as a measure of the denticity of borohydride groups, values of

Table 1. Key structural parameters of compounds **1**^{c}–**10**^{c} and **12**. In cases where the EPB fragment is disordered over two positions (E = O, S, Se, Te), the structural parameters of the molecule at the position with higher occupancy are given.

		P–E [Å]	P–B [Å]	P–C[a] [Å]	C–P–C′ [°]	K–P/E [Å]	K···B [Å]	K–E–P [°]
1^{c}	$[K(18\text{-c-}6)][PPh_2BH_3]$	–	1.960(6)	1.843(6)	101.2(2)	3.320(2)	3.162	–
2^{c}	$[K(18\text{-c-}6)][OPPh_2BH_3]$	1.514(1)	1.908(2)	1.832(1)	100.4(1)	2.742(1)	3.583	104.2(1)
3^{c}	$[K(18\text{-c-}6)][SPPh_2BH_3]$	1.987(4)	1.972(5)	1.822(9)	101.9(4)	3.365(4)	3.273	89.7(1)
4^{c}	$[K(18\text{-c-}6)][SePPh_2BH_3]$	2.182(1)	1.907(6)	1.828(2)	102.3(1)	3.491(1)	3.266	87.6(1)
5^{c}	$[K(18\text{-c-}6)][TePPh_2BH_3]$	2.398(1)	1.921(6)	1.830(2)	102.5(1)	3.680(1)	3.408	85.2(1)
6^{c}	$[K(18\text{-c-}6)][PtBu_2BH_3]$	–	1.956(12)[b]	1.882(12)[b]	109.7(5)[b]	4.92/4.94	3.029/3.133	–
7^{c}	$[K(18\text{-c-}6)][OPtBu_2BH_3]$	1.525(2)	1.932(4)	1.879(2)	110.8(1)	2.524(2)	4.683	149.5(1)
8^{c}	$[K(18\text{-c-}6)][SPtBu_2BH_3]$	2.011(1)	1.948(2)	1.880(2)	111.0(1)	3.297(1)	3.751	96.2(1)
9^{c}	$[K(18\text{-c-}6)][SePtBu_2BH_3]$	2.161(1)	1.982(3)	1.882(3)	111.0(2)	3.413(1)	4.114	97.3(1)
10^{c}	$[K(18\text{-c-}6)][TePtBu_2BH_3]$	2.412(1)	2.141(2)	1.889(2)	111.1(1)	3.796(1)	3.698	83.2(1)
12	$OPPh_2CH_3$	1.494(2)	–	1.808(3)[c]	105.1(1)[d]	–	–	–

[a] Mean value. [b] Mean value of the two crystallographically independent molecules. [c] P–C(phenyl). [d] C(phenyl)–P–C′(phenyl).

1.6 ± 0.1 and 1.36 ± 0.06 Å are estimated for the ionic radii of didentate and tridentate borohydride ligands, respectively. Deduction of an effective ionic radius of a unidentate BH_4^- group is less straightforward, however, mainly because of the greater flexibility of the M–H–B linkage (cf. $r(BH_4^-)$ = 2.23 Å in $[Fe(\eta^1\text{-}BH_4)H(dmpe)_2]$;[20] $r(BH_4^-)$ = 1.92 Å in $[Cu(\eta^1\text{-}BH_4)(PPh_2Me)_3]$[20,21]). However, it has been suggested that if subtraction of the metal ionic radius from the M···B distance in a tetrahydroborate complex gives a value of 1.8 Å or greater, it is likely that the BH_4^- ligand is unidentate.[20] These data lead to the conclusion that K···B distances of about 3.5, 3.25 and 3.01 Å are to be expected for mono-, di and tridentate coordination modes, respectively (ionic radius of octacoordinate K^+ = 1.65 Å[22]).

We start our discussion of the molecular structures with a comparison of the two parent phosphanylborohydrides $[K(18\text{-c-}6)][PPh_2BH_3]$ (**1**^{c}; Figure 1) and $[K(18\text{-c-}6)][PtBu_2BH_3]$ (**6**^{c}; Figure 2) which differ substantially in the steric demand of their organyl substituents. The K–P contact in compound **1**^{c} amounts to 3.320(2) Å and is thus significantly shorter than the sum (3.55 Å) of the van der Waals radius of phosphorus (1.9 Å[23]) and the ionic radius of K^+ [angle K–P–B = 68.1(2)°]. The corresponding K···B distance (3.162 Å) suggests an additional η^2-coordination of the BH_3 fragment. In contrast to **1**^{c}, the K–P distances of 4.92 and 4.94 Å in **6**^{c} (two crystallographically independent molecules in the asymmetric unit) and K–B–P angles of 149° and 166° clearly exclude any bonding interaction between K^+ and the electron lone-pair at phosphorus. Similar to **1**^{c}, **6**^{c} features short K···B contacts in the solid state (3.133 and 3.029 Å). In one of the two molecules, K–B coordination is therefore somewhere between η^2 and η^3, whereas the second ion-pair is linked by an η^3-coordinated BH_3 fragment. The differences between the solid-state

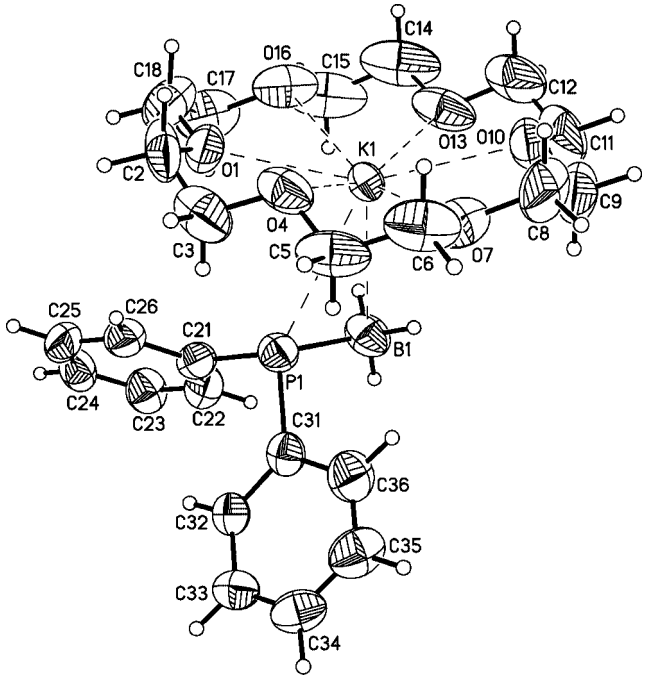


Figure 1. Molecular structure and numbering scheme of compound **1**^{c}; thermal ellipsoids shown at the 50% probability level.

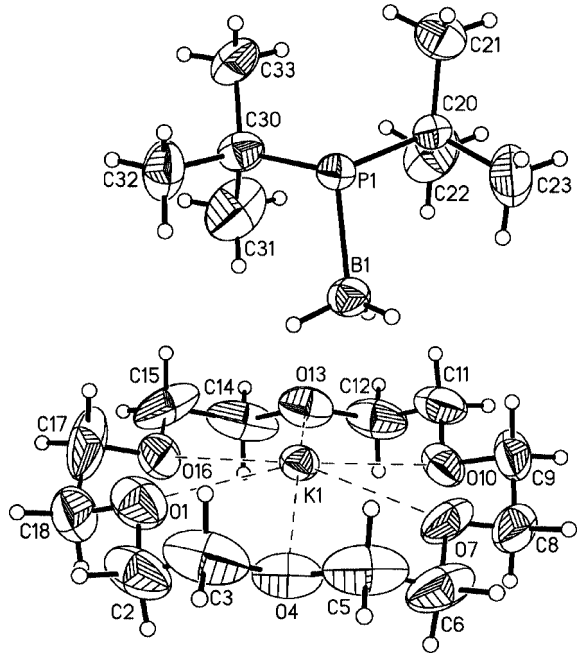


Figure 2. Molecular structure and numbering scheme of compound **6**^{c}; thermal ellipsoids shown at the 50% probability level. Only one of the two crystallographically independent $[K(18\text{-c-}6)][PtBu_2BH_3]$ units is shown.

structures of **1**[c] and **6**[c] clearly originate from the fact that the bulky *tert*-butyl substituents in the latter compound force the phosphorus centre away from the $[K(18\text{-c-}6)]^+$ plane.

The $[EPPh_2BH_3]^-$ anions of **2**[c]–**5**[c] all coordinate to the K^+ ion through both their chalcogen atom and their BH_3 groups (η^2 in the case of the sulfur and selenium derivatives **3**[c] and **4**[c], η^1 mode in the case of the oxygen and tellurium derivatives **2**[c] and **5**[c]; cf. K···B distances in Table 1). Replacement of phenyl by *tert*-butyl substituents (**7**[c]–**10**[c]) leads to longer K···B distances but shorter K–E bonds (the only exception is the K–Te bond of **10**[c], which is somewhat longer than the K–Te bond in **5**[c]). Provided that the steric requirements are met, as in the case of **2**[c]–**5**[c], it is thus apparent that BH_3 coordination to the K^+ ion can successfully compete with chalcogen binding. Even though the steric demand of two *tert*-butyl substituents in **7**[c]–**10**[c] precludes the close approach between K^+ and B required for the formation of 3c–2e KHB bonds, we nevertheless assume a significant electrostatic attraction between the negative partial charge residing on the BH_3 unit and the K^+ cation in the *tert*-butyl derivatives as well. As representative examples the molecular structures of $[K(18\text{-c-}6)][OPPh_2BH_3]$ (**2**[c]), $[K(18\text{-c-}6)][OPtBu_2BH_3]$ (**7**[c]), $[K(18\text{-c-}6)][TePPh_2BH_3]$ (**5**[c]) and $[K(18\text{-c-}6)][TePtBu_2BH_3]$ (**10**[c]) are shown in Figures 3, 4, 5 and 6, respectively.

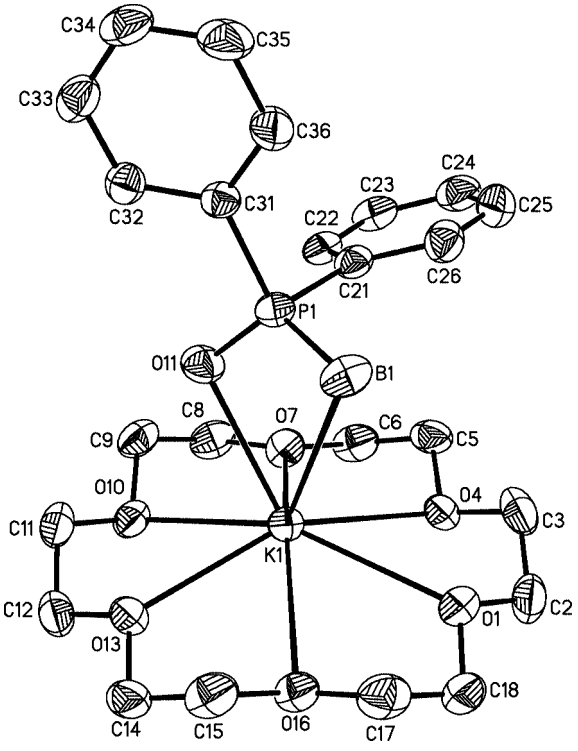


Figure 3. Molecular structure and numbering scheme of compound **2**[c]; thermal ellipsoids shown at the 50% probability level; hydrogen atoms omitted for clarity.

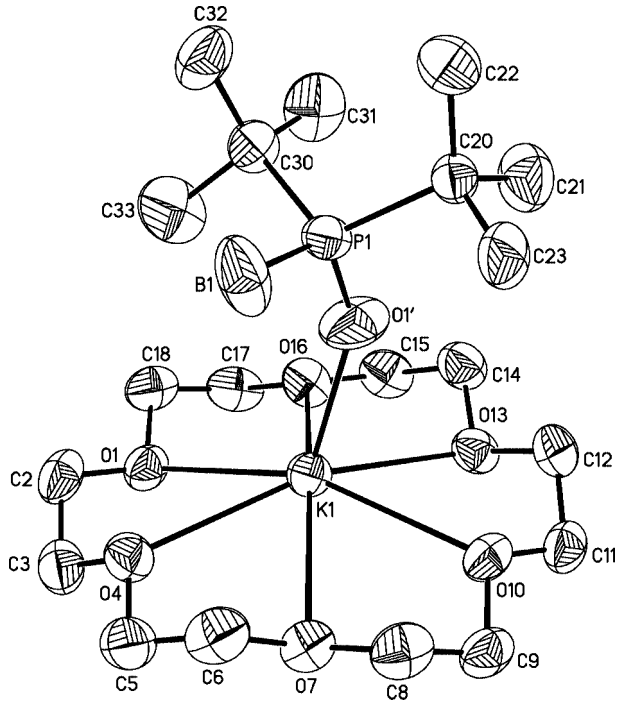


Figure 4. Molecular structure and numbering scheme of compound **7**[c]; thermal ellipsoids shown at the 50% probability level; hydrogen atoms omitted for clarity.

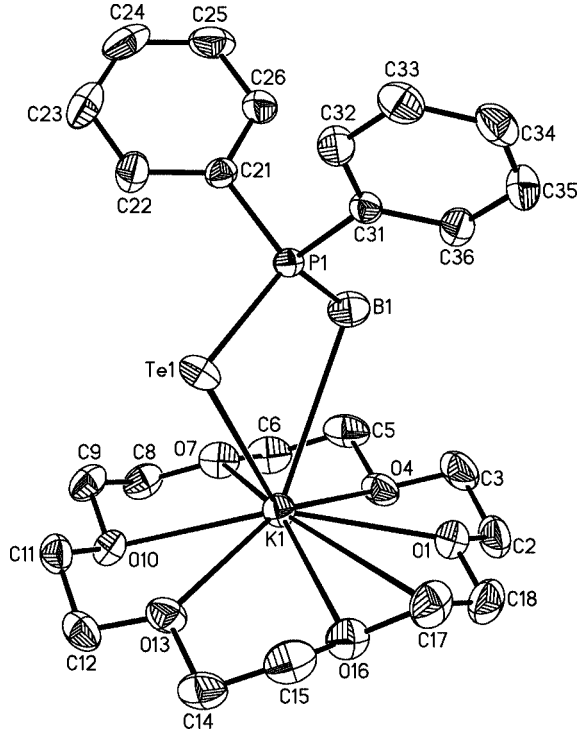


Figure 5. Molecular structure and numbering scheme of compound **5**[c]; thermal ellipsoids shown at the 50% probability level; hydrogen atoms omitted for clarity.

The vast majority of M–E–P angles in metal complexes of chalcogenophosphorylic ligands either fall in the range between 180° and 140° ($L_nM\text{-}OPR_3$) or 115° and 98° ($L_nM\text{-}EPR_3$; E = S, Se).[24] A similar trend is observed for our $[K(18\text{-c-}6)][EPR_2BH_3]$ derivatives in that the largest K–E–P angle within each of the two series is established by the oxo species. However, the *absolute* values of the K–E–P angles in $[K(18\text{-c-}6)][EPR_2BH_3]$ are generally much smaller

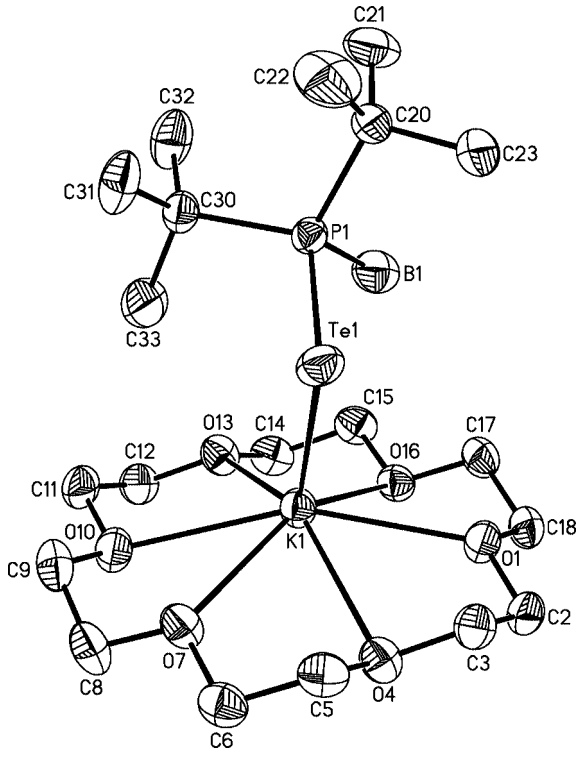


Figure 6. Molecular structure and numbering scheme of compound **10**^{c}; thermal ellipsoids shown at the 50% probability level; hydrogen atoms omitted for clarity.

than those of the corresponding M–E–P angles in L_nM-EPR_3, which is most likely the result of the auxiliary K–H_3B interaction discussed above.

Looking at the series of compounds **2**^{c}–**5**^{c} and **7**^{c}–**10**^{c} as well as at related triorganylphosphane chalcogenides, it is our goal to find out whether differences in the electron density distribution at phosphorus can be correlated to systematic trends in key structural parameters such as the E–P and P–C bond lengths or the C–P–C′ bond angles. For example, it is generally accepted[25] that 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.

A comparison of E–P bond lengths in **2**^{c}–**5**^{c} with those of related molecules **7**^{c}–**10**^{c} reveals larger E–P distances in the *tert*-butyl derivatives **7**^{c}, **8**^{c} and **10**^{c} (Table 1). However, the differences are very small, and in the case of the Se compounds the order is even reversed (**9**^{c} < **4**^{c}). Our negatively charged molecules $[EPPh_2BH_3]^-$ possess slightly longer E–P bonds than comparable neutral triorganophosphane chalcogenides (Table 2). This effect may either result from K^+ coordination[26] or from the presence of the electron-releasing BH_3 fragment in **2**^{c}–**5**^{c}. Irrespective of whether E→P backbonding via *negative hyperconjugation* or electrostatic attraction in a highly polar $^{-}E\text{-}^{+}PR_3$ adduct is the more adequate description of the E–P bond, both factors are likely less pronounced in compounds $K(EPR_2BH_3)$ than in EPR_2CH_3 as a consequence of the more negative formal charge on phosphorus in the BH_3-containing molecules. Correlations between the length of a polar bond determined in the solid state and the bond strength or bond order must, however, not be overemphasised because crystal packing effects also have to be taken into consideration. An interesting trend is evident for the C(phenyl)–P–C′(phenyl) angles, which are significantly more acute in the ionic species **2**^{c}, **3**^{c} and **4**^{c} than in the neutral triorganophosphane chalcogenides (Table 2). Replacement of one organyl substituent by the BH_3 group thus results in an increased p character of the two remaining P–C(phenyl) bonds, which is in agreement with the isovalent hybridisation hypothesis.[25] This conclusion is further supported by the fact that the P–C(phenyl) bond is considerably longer in **2**^{c} [1.832(1) Å] than in $OPPh_2CH_3$ [**12**; 1.808(3) Å]. In the case of the heavier homologues **3**^{c}/$SPPh_3$ and **4**^{c}/$SePPh_3$, however, this bond length difference is levelled out to such an extent that it is no longer of diagnostic significance (Table 2).

Table 2. Comparison of the ionic species **2**^{c}, **3**^{c}, **4**^{c}, and **5**^{c} with their triorganyl analogues.

		P–E [Å]	P–C[a] [Å]	C–P–C′ [°]
2^{c}	$[K(18\text{-c-}6)][OPPh_2BH_3]$	1.514(1)	1.832(1)	100.4(1)
12	$OPPh_2CH_3$	1.494(2)	1.808(3)	105.1(1)
3^{c}	$[K(18\text{-c-}6)][SPPh_2BH_3]$	1.987(4)	1.822(9)	101.9(4)
	$SPPh_3$[b]	1.950(3)	1.817(8)	105.7(6)[a]
4^{c}	$[K(18\text{-c-}6)][SePPh_2BH_3]$	2.182(1)	1.828(2)	102.3(1)
	$SePPh_3$[c]	2.106(1)	1.826(10)	105.7(7)[a]
5^{c}	$[K(18\text{-c-}6)][TePPh_2BH_3]$	2.398(1)	1.830(2)	102.5(1)
	$TeP\textit{i}Pr_3$[d]	2.363(1)	–	–
	$TeP\textit{t}Bu_3$[e]	2.368(4)		

[a] Mean value. [b] Ref.[45] [c] Ref.[46] [d] Ref.[47] [e] Ref.[48]

NMR Spectroscopy

Characteristic NMR parameters of compounds **1**–**15** (Scheme 1) are compiled in Table 3. For comparability and solubility reasons, all NMR spectra were recorded at 300 K for thf solutions.

The phosphanylborohydrides $K(PPh_2BH_3)$ (**1**) and $K(P\textit{t}Bu_2BH_3)$ (**6**) possess ^{31}P NMR shifts of δ = –28.8 and 12.8 ppm, respectively, remarkably close to the values of the isoelectronic triorganylphosphanes PPh_2CH_3 (**11**; δ = –26.1 ppm[12]) and $P\textit{t}Bu_2CH_3$ (δ = 11.3 ppm). The pronounced deshielding of the ^{31}P NMR resonance upon going from the phenyl to the *tert*-butyl derivatives is attributable to the high steric demand of the alkyl substituents, which enforces a widening of the C–P–C′ angles by an increased admixture of the 3s orbital to the P–C bond.[18] As a consequence, the phosphorus lone-pair is depleted of s character and, in turn, loses some of its shielding effect. In the case of the tetra-coordinated chalcogen compounds the ^{31}P NMR resonances of the phenyl derivatives **2**–**5** also appear at higher field than the signals of the corresponding *tert*-butyl derivatives **7**–**10**. The shift difference lies between 30.0 ppm (**2/7**) and 64.6 ppm (**5/10**). We also note that varying the chalcogeno substituent has a much more pronounced effect on the resonance frequency of the ^{31}P nucleus in the

Table 3. Selected NMR parameters of compounds **1**–**15** in thf; upfield shifts are denoted by a minus sign and downfield shifts by a plus sign.

	Nucleus	δ [ppm] (^1J [Hz])				
		^{31}P	^{11}B ($^1J_{P,B}$)	E ($^1J_{PE}$)	P-$^{13}C_i$ ($^1J_{P,C}$)	P-^{13}CH$_3$ ($^1J_{P,C}$)
1	K(PPh$_2$BH$_3$)	–28.8	–30.1 (32.1)	–	150.2 (20.1)	–
2	K(OPPh$_2$BH$_3$)	64.0	–35.7 (98.7)	–	145.4 (54.0)	–
3	K(SPPh$_2$BH$_3$)	42.1	–31.3 (78.2)	–	143.3 (44.3)	–
4	K(SePPh$_2$BH$_3$)	21.8	–30.3 (67.0)	–264.5 (544)	141.3 (40.1)	–
5	K(TePPh$_2$BH$_3$)	–30.9	–28.1 (51.2)	–509.3 (1249)	139.6 (35.5)	–
6	K(P*t*Bu$_2$BH$_3$)	12.8	–34.7 (33.8)	–	32.4 (12.5)	–
7	K(OP*t*Bu$_2$BH$_3$)	94.0	–39.4 (100.6)	–	34.8 (30.1)	–
8	K(SP*t*Bu$_2$BH$_3$)	76.6	–35.3 (80.8)	–	35.2 (21.6)	–
9	K(SeP*t*Bu$_2$BH$_3$)	68.4	–34.4 (72.9)	–379.8 (514)	34.0 (17.0)	–
10	K(TeP*t*Bu$_2$BH$_3$)	33.7	–32.2 (64.3)	–782.0 (1170)	32.4 (12.5)	–
11	PPh$_2$CH$_3$	–26.1	–	–	140.8 (10.0)	12.9 (12.0)
12	OPPh$_2$CH$_3$	28.3	–	–	135.8 (99.8)	16.2 (73.2)
13	SPPh$_2$CH$_3$	35.8	–	–	135.7 (81.2)	21.4 (60.1)
14	SePPh$_2$CH$_3$	24.3	–	–305.7 (744)	134.4 (73.1)	21.9 (53.3)
15	TePPh$_2$CH$_3$	25.6	–	–554.5 (s)	–	–

borohydride derivatives **2**–**5** and **7**–**10** than in the triorganophosphane chalcogenides **12**–**15** (Table 3).

The ^{11}B NMR shifts of **1**–**10** range from δ = –28.1 (**5**) to –39.4 ppm (**7**) and are typical of phosphane–borane adducts.[27]

$^1J_{P,X}$ coupling constants are valuable diagnostic tools for an assessment of the degree of s character in the P–X bonding orbitals (X = B, C, Se, Te).[28] In many cases, linear correlations between both parameters have been established. This can easily be rationalised if we assume that NMR coupling constants via a certain bond are governed by the Fermi contact term, which increases with increasing s orbital admixture to the respective bond.[28] Moreover, the magnitude of $^1J_{P,B}$ coupling constants in phosphane–borane adducts serves as a qualitative measure of the strength of the P–B bond.[13,29–31] Looking at the coupling constants via the P–B ($^1J_{P,B}$), P–CH$_3$ ($^1J_{P,C}$) and P–C(phenyl) bonds ($^1J_{P,Ci}$), there is always the same qualitative trend: all these coupling constants increase substantially upon attachment of chalcogeno substituents to the phosphorus centres of the parent molecules K(PPh$_2$BH$_3$) (**1**), K(P*t*Bu$_2$BH$_3$) (**6**) and PPh$_2$CH$_3$ (**11**). This effect is strongest for the oxo systems **2**, **7** and **12** and decreases monotonously along the series O > S > Se > Te. From these data it becomes evident that P–E bond formation is accompanied by an increase in s character of the P–BH$_3$/P–CH$_3$ and P–C(phenyl) bonds. Concomitantly, the former phosphorus lone-pair gains p character as it becomes involved in covalent bonding to the chalcogen atom. In line with Bent's rule,[25] this gain is most pronounced for compounds containing the chalcogen atom of highest electronegativity (O); it is intermediate for S and Se and least pronounced for the chalcogen atom of lowest electronegativity (Te). Interestingly, the $^1J_{P,X}$ values of the sulfur derivatives **3**, **8** and **13** are consistently larger than those of the corresponding Se-containing species **4**, **9** and **14** even though the electronegativity of S (χ = 2.44[23]) is *smaller* than the electronegativity of Se (χ = 2.48[23]). It is thus obvious that additional effects have to be taken into account for a more detailed understanding of trends in the $^1J_{P,X}$ constants and that the degree of E→P π backbonding in particular must not be neglected. Differences in the $^1J_{P,B}$ values of species K(EPPh$_2$BH$_3$) and K(EP*t*Bu$_2$BH$_3$) bearing the same kind of atom E become larger with increasing atomic number of E. Thus, the influence of the organic substituents on the strength of the P–B bond is smallest in the oxo derivatives and most pronounced in the tellurium species.

The ^{77}Se and ^{125}Te NMR spectra of **4**, **5**, **9**, **10**, **14** and **15**[32] were measured and the data included in Table 3. Triorganophosphane selenides are known to possess $^1J_{P,Se}$ coupling constants in the range between 700 and 1100 Hz.[28] For SePPh$_2$CH$_3$ (**14**) we have determined a chemical shift value of –305.7 ppm with a $^1J_{P,Se}$ coupling constant of 744 Hz. Formal replacement of CH$_3$ by BH$_3$ (**14** → **4**) leads to a downfield shift of the ^{77}Se resonance by 41.2 ppm (**4**: δ = –264.5 ppm) together with a decrease of the absolute value of the coupling constant by 200 Hz (**4**: $^1J_{P,Se}$ = 544 Hz).

Conclusions

Two complete series of chalcogenated phosphanylborohydrides K(EPR$_2$BH$_3$) (E = O-Te; R = Ph, *t*Bu) have been synthesised and all compounds investigated by NMR spectroscopy and X-ray crystallography (in the latter case as 18-crown-6 adducts). In all cases the molecules contain a P–B bond and there is no migration of BH$_3$ from the phosphorus to the chalcogen atom. A comparison of characteristic structural [e.g. E–P bond lengths, C(phenyl)–P–C′(phenyl) bond angles] and NMR spectroscopic (e.g. $^1J_{P,X}$ coupling constants; X = B, C, Se, Te) parameters of the isoelectronic and isostructural species [EPPh$_2$BH$_3$]$^-$ and EPPh$_2$CH$_3$ leads to the conclusion that [PPh$_2$BH$_3$]$^-$ directs a σ orbital of higher p character towards the respective chalcogen atom than PPh$_2$CH$_3$. All trends in the above mentioned parameters are nicely correlated to the changes in the electronegativities of the atoms E, as predicted by

Bent's rule.[25] We have already found similar correlations in pure σ adducts of $[PPh_2BH_3]^-$ and PPh_2CH_3,[12] which leads us to the conclusion that no influence of E→P backbonding is discernible in our study.

All structural and NMR spectroscopic data indicate the E–P bonds to be stronger with $[PPh_2BH_3]^-$ than with PPh_2CH_3 as ligand. This conclusion is supported by the fact that the telluride $K(TePPh_2BH_3)$ is isolable in good yield whereas $TePPh_2CH_3$ forms from a thf solution of PPh_2CH_3 and Te_∞ only in trace amounts in a dynamic equilibrium. Moreover, displacement experiments between $K(PPh_2BH_3)$ and $EPPh_2CH_3$ (E = S, Se) resulted in the quantitative formation of $K(EPPh_2BH_3)$ and PPh_2CH_3. A similar reaction between $K(PPh_2BH_3)$ and $OPPh_2CH_3$ does not take place (thf, 65 °C, 18 h), most likely due to kinetic rather than thermodynamic reasons. As in triorganylphosphanes the *tert*-butyl derivative $[PtBu_2BH_3]^-$ appears to be an even better Lewis base than its counterpart $[PPh_2BH_3]^-$, most likely for both electronic (+I effect of alkyl substituents) and steric (widening of the C–P–C angle due to steric crowding) reasons.

From an inspection of the molecular structures of [K(18-c-6)][$EPPh_2BH_3$] it becomes evident that $[EPPh_2BH_3]^-$ ligands have to be considered as potentially chelating, with one donor site being the chalcogen atom E and the second the BH_3 moiety, which can bind to a metal centre through its hydride substituents. We are presently systematically exploring the potential of phosphanylborohydrides as anionic analogues of triorganophosphanes in coordination chemistry.

Experimental Section

General Considerations: All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of 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, DPX 250, AV 300 and AV 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 (C_6D_5H: δ = 7.16, C_6D_6: δ = 128.06 ppm; $CHCl_3$: δ = 7.26, $CDCl_3$: δ = 77.16 ppm).[33] ^{11}B NMR spectra were referenced against external $BF_3{\cdot}OEt_2$, ^{31}P NMR spectra against external H_3PO_4 (85%) and ^{77}Se NMR spectra against external concentrated aqueous H_2SeO_3 (δ = 1300 ppm vs. Me_2Se).[34] ^{125}Te NMR spectra were referenced against external concentrated aqueous H_6TeO_6 (δ = 712 ppm vs. Me_2Te).[35] Abbreviations: s = singlet, d = doublet, q = quartet, dq = doublet of quartets, m = multiplet, n.r. = multiplet expected in the NMR spectrum but not resolved, *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, PPh_3, PPh_2CH_3, $PtBu_2H$, KH, N_2O, S_8, Se_∞, Te_∞, $BH_3{\cdot}THF$ solution (1 M in thf) and 18-crown-6 were purchased from Aldrich or Fluka and used as received. $HPPh_2$ was obtained by reductive cleavage of triphenylphosphane with lithium powder in thf and subsequent hydrolysis and distillation following a literature procedure.[36] The BH_3 adduct $HPPh_2BH_3$ was synthesised as described previously.[12] The same procedure was also used to make $HPtBu_2BH_3$.[37] The phosphane chalcogenides $EPPh_2CH_3$ (**12**–**15**) were synthesised by the reaction of PPh_2CH_3 with H_2O_2, S_8, grey Se_∞ or Te_∞ in thf at room temperature.[38–40] $TePPh_2CH_3$ could not be obtained in pure form; the ^{31}P NMR spectrum of the yellow reaction mixture showed a yield of approximately 6% of the target compound (dynamic equilibrium between $TePPh_2CH_3$, Te_∞ and PPh_2CH_3).

Synthesis of $K(PPh_2BH_3)$ (1): A solution of $HPPh_2BH_3$ (2.29 g, 11.4 mmol) in thf (5 mL) was added to a suspension of KH (480 mg, 12.0 mmol) in thf (10 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight. After filtration from residual KH, all volatiles were removed in vacuo. The resulting yellow oily residue solidified upon treatment with pentane. Yield: 2.40 g (88%). ^1H NMR (thf, 250.13 MHz): δ = 0.9 (m, 3 H, BH_3), 6.79–6.87 (m, 2 H, H-*p*), 6.90–6.98 (m, 4 H, H-*m*), 7.41–7.49 (m, 4 H, H-*o*) ppm. ^{11}B NMR (thf, 128.38 MHz): δ = –30.1 ppm (dq, $^1J_{P,B}$ = 32.1, $^1J_{B,H}$ = 89.9 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 124.5 (n.r., C-*p*), 127.0 (d, $^3J_{P,C}$ = 5.1 Hz, C-*m*), 133.9 (d, $^2J_{P,C}$ = 14.0 Hz, C-*o*), 150.2 (d, $^1J_{P,C}$ = 20.1 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = –28.8 ppm (m). $C_{24}H_{37}BKO_6P$ (502.42): calcd. C 57.37, H 7.42; found C 57.25, H 7.39.

Synthesis of $K(OPPh_2BH_3)$ (2): A solution of **1** (479 mg, 2.01 mmol) in thf (5 mL) was stirred at room temp. under an atmosphere of N_2O until the gas evolution had entirely stopped and the pale-yellow colour had disappeared (ca. 5 min). All volatiles were then removed in vacuo to give a colourless crystalline solid. Yield: 500 mg (98%). ^1H NMR (thf, 250.13 MHz): δ = 0.9 (m, 3 H, BH_3), 7.03–7.13 (m, 6 H, H-*m*,*p*), 7.64–7.75 (m, 4 H, H-*o*) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –35.7 ppm (d, $^1J_{P,B}$ = 98.7 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 127.8 (d, $^3J_{P,C}$ = 8.4 Hz, C-*m*), 128.7 (n.r., C-*p*), 130.7 (d, $^2J_{P,C}$ = 9.9 Hz, C-*o*), 145.4 (d, $^1J_{P,C}$ = 54.0 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 101.25 MHz): δ = 64.0 ppm (m). $C_{24}H_{37}BKO_7P$ (518.42): calcd. C 55.60, H 7.19; found C 55.65, H 7.20.

Synthesis of $K(SPPh_2BH_3)$ (3): A solution of **1** (476 mg, 2.00 mmol) in thf (5 mL) was added to a suspension of S_8 (70 mg, 2.18 mmol S_1) in thf (6 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight. All volatiles were removed in vacuo and the resulting pale-yellow solid was triturated with toluene (2 × 5 mL). Yield: 513 mg (95%). ^1H NMR (thf, 250.13 MHz): δ = 1.3 (m, 3 H, BH_3), 7.20–7.30 (m, 6 H, H-*m*,*p*), 8.11–8.23 (m, 4 H, H-*o*) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –31.3 ppm (d, $^1J_{P,B}$ = 78.2 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 127.3 (d, $^3J_{P,C}$ = 9.6 Hz, C-*m*), 128.2 (d, $^4J_{P,C}$ = 2.4 Hz, C-*p*), 131.8 (d, $^2J_{P,C}$ = 10.1 Hz, C-*o*), 143.3 (d, $^1J_{P,C}$ = 44.3 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 42.1 ppm (m). $C_{24}H_{37}BKO_6PS$ (534.48): calcd. C 53.93, H 6.98; found C 53.34, H 6.52.

Synthesis of $K(SePPh_2BH_3)$ (4): A solution of **1** (500 mg, 2.10 mmol) in thf (5 mL) was added with stirring at –78 °C to a suspension of grey Se_∞ (166 mg, 2.10 mmol Se_1) in thf (2 mL). The mixture was warmed to room temp. overnight whereupon the Se_∞ completely dissolved. All volatiles were then removed in vacuo. The resulting pale-yellow solid was triturated with pentane (2 mL). Yield: 613 mg (92%). ^1H NMR (thf, 250.13 MHz): δ = 1.4 (m, 3 H, BH_3), 6.95–7.11 (m, 6 H, H-*m*,*p*), 7.93–8.05 (m, 4 H, H-*o*) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –30.3 ppm (d, $^1J_{P,B}$ = 67.0 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 127.3 (d, $^3J_{P,C}$ = 9.6 Hz, C-*m*), 128.5 (n.r., C-*p*), 132.5 (d, $^2J_{P,C}$ = 10.0 Hz, C-*o*),

141.3 (d, $^1J_{P,C}$ = 40.1 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 21.8 ppm (m). ^{77}Se NMR (thf, 47.69 MHz): δ = –264.5 ppm (d, $^1J_{P,Se}$ = 544 Hz). $C_{24}H_{37}BKO_6PSe$ (581.38): calcd. C 49.58, H 6.41; found C 49.11, H 6.03.

Synthesis of K(TePPh$_2$BH$_3$) (5): A solution of **1** (414 mg, 1.74 mmol) in thf (6 mL) was added to a suspension of Te$_\infty$ (222 mg, 1.74 mmol Te$_1$) in thf (4 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight. The resulting yellow solution was filtered and all volatiles removed in vacuo. The remaining yellow solid was triturated with pentane (2 mL). Yield: 605 mg (95%). ^1H NMR (thf, 250.13 MHz): δ = 1.8 (m, 3 H, BH$_3$), 6.93–7.09 (m, 6 H, H-*m*,*p*), 7.89–8.00 (m, 4 H, H-*o*) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –28.1 ppm (d, $^1J_{P,B}$ = 51.2 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 127.3 (d, $^3J_{P,C}$ = 9.5 Hz, C-*m*), 128.5 (n.r., C-*p*), 133.5 (d, $^2J_{P,C}$ = 9.6 Hz, C-*o*), 139.6 (d, $^1J_{P,C}$ = 35.5 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = –30.9 ppm (m). $^{125}Te\{^1H\}$ NMR (thf, 78.88 MHz): δ = –509.3 ppm (d, $^1J_{P,Te}$ = 1249 Hz). $C_{24}H_{37}BKO_6PTe$ (630.02): calcd. C 45.75, H 5.92; found C 45.53, H 5.65.

Synthesis of K(P*t*Bu$_2$BH$_3$) (6): A solution of HP*t*Bu$_2$BH$_3$ (1.14 g, 7.12 mmol) in thf (5 mL) was added to a suspension of KH (290 mg, 7.23 mmol) in thf (6 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight. After filtration from residual KH all volatiles were removed in vacuo. Yield: 1.15 g (82%). ^1H NMR (thf, 250.13 MHz): δ = 0.28 (q, $^1J_{B,H}$ = 88 Hz, 3 H, BH$_3$), 1.16 (d, $^3J_{P,H}$ = 9.8 Hz, 18 H, CH$_3$) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –34.7 ppm (d, $^1J_{P,B}$ = 33.8 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 29.6 (d, $^2J_{P,C}$ = 2.8 Hz, CH$_3$), 32.4 (d, $^1J_{P,C}$ = 12.5 Hz, *C*CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 12.8 ppm (m). $C_{20}H_{45}BKO_6P$ (462.44): calcd. C 51.94, H 9.81; due to the extreme air and moisture sensitivity of the compound a decent elemental analysis was not obtained, even from a single crystalline sample.

Synthesis of K(OP*t*Bu$_2$BH$_3$) (7): A solution of **6** (240 mg, 1.21 mmol) in thf (3 mL) was stirred at room temp. under an atmosphere of N_2O until the gas evolution had entirely stopped (ca. 5 min). After all volatiles had been removed in vacuo, the product was obtained as a colourless crystalline solid. Yield: 255 mg (98%). ^1H NMR (thf, 250.13 MHz): δ = 0.4 (m, 3 H, BH$_3$), 1.14 (d, $^3J_{P,H}$ = 11.2 Hz, 18 H, CH$_3$) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –39.4 ppm (d, $^1J_{P,B}$ = 100.6 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 27.8 (d, $^2J_{P,C}$ = 2.3 Hz, CH$_3$), 34.8 (d, $^1J_{P,C}$ = 30.1 Hz, *C*CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 94.0 ppm (m). $C_{20}H_{45}BKO_7P$ (478.44): calcd. C 50.21, H 9.48; found C 49.97, H 9.58.

Synthesis of K(SP*t*Bu$_2$BH$_3$) (8): A solution of **6** (283 mg, 1.43 mmol) in thf (3 mL) was added to a suspension of S$_8$ (48 mg, 1.50 mmol S$_1$) in thf (3 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight. After all volatiles had been removed in vacuo, the resulting colourless solid was triturated with pentane (2 × 2 mL). Yield: 322 mg (98%). ^1H NMR (thf, 300.03 MHz): δ = 0.52 (q, $^1J_{B,H}$ = 92 Hz, 3 H, BH$_3$), 1.19 (d, $^3J_{P,H}$ = 12.0 Hz, 18 H, CH$_3$) ppm. $^{11}B\{^1H\}$ NMR (thf, 96.26 MHz): δ = –35.3 ppm (d, $^1J_{P,B}$ = 80.8 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 28.5 (d, $^2J_{P,C}$ = 2.9 Hz, CH$_3$), 35.2 (d, $^1J_{P,C}$ = 21.6 Hz, *C*CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (thf, 121.46 MHz): δ = 76.6 ppm (q, $^1J_{P,B}$ = 80.8 Hz). $C_{20}H_{45}BKO_6PS$ (494.50): calcd. C 48.58, H 9.17; found C 48.68, H 9.23.

Synthesis of K(SeP*t*Bu$_2$BH$_3$) (9): A solution of **6** (279 mg, 1.41 mmol) in thf (3 mL) was added to a suspension of grey Se$_\infty$ (111 mg, 1.41 mmol Se$_1$) in thf (2 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight, whereupon the Se$_\infty$ dissolved completely. The reaction mixture was evaporated to dryness in vacuo and the resulting colourless solid triturated with pentane (2 mL). Yield: 357 mg (91%). ^1H NMR (thf, 250.13 MHz): δ = 0.75 (q, $^1J_{B,H}$ = 93 Hz, 3 H, BH$_3$), 1.27 (d, $^3J_{P,H}$ = 12.6 Hz, 18 H, CH$_3$) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –34.4 ppm (d, $^1J_{P,B}$ = 72.9 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 29.0 (d, $^2J_{P,C}$ = 3.0 Hz, CH$_3$), 34.0 (d, $^1J_{P,C}$ = 17.0 Hz, *C*CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 68.4 ppm (m). ^{77}Se NMR (thf, 76.30 MHz): δ = –379.8 ppm (d, $^1J_{P,Se}$ = 514 Hz). $C_{20}H_{45}BKO_6PSe$ (541.40): calcd. C 44.37, H 8.38; found C 44.35, H 8.50.

Synthesis of K(TeP*t*Bu$_2$BH$_3$) (10): A solution of **6** (302 mg, 1.52 mmol) in thf (3 mL) was added to a suspension of Te$_\infty$ (195 mg, 1.53 mmol Te$_1$) in thf (3 mL) with stirring at –78 °C. The mixture was then warmed to room temp. overnight. The resulting yellow solution was filtered and all volatiles removed in vacuo. The yellow solid residue was triturated with pentane (2 × 2 mL). Yield: 490 mg (99%). ^1H NMR (thf, 250.13 MHz): δ = 1.2 (m, 3 H, BH$_3$), 1.34 (d, $^3J_{P,H}$ = 12.8 Hz, 18 H, CH$_3$) ppm. $^{11}B\{^1H\}$ NMR (thf, 128.38 MHz): δ = –32.2 ppm (d, $^1J_{P,B}$ = 64.3 Hz). $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 29.6 (d, $^2J_{P,C}$ = 2.8 Hz, CH$_3$), 32.4 (d, $^1J_{P,C}$ = 12.5 Hz, *C*CH$_3$) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 33.7 ppm (m). $^{125}Te\{^1H\}$ NMR (thf, 78.88 MHz): δ = –782.0 (d, $^1J_{P,Te}$ = 1170 Hz). $C_{20}H_{45}BKO_6PTe$ (590.04): calcd. C 40.71, H 7.69; found C 40.38, H 7.27.

OPPh$_2$CH$_3$ (12): ^1H NMR (thf, 400.13 MHz): δ = 1.80 (d, $^2J_{P,H}$ = 13.4 Hz, 3 H, CH$_3$), 7.20–7.30 (m, 6 H, H-*m*,*p*), 7.66–7.74 (m, 4 H, H-*o*) ppm. $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 16.2 (d, $^1J_{P,C}$ = 73.2 Hz, CH$_3$), 128.8 (d, $^3J_{P,C}$ = 11.7 Hz, C-*m*), 130.9 (d, $^2J_{P,C}$ = 9.6 Hz, C-*o*), 131.6 (d, $^4J_{P,C}$ = 2.8 Hz, C-*p*), 135.8 (d, $^1J_{P,C}$ = 99.8 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 28.3 ppm (s).

SPPh$_2$CH$_3$ (13): ^1H NMR (thf, 250.13 MHz): δ = 2.04 (d, $^2J_{P,H}$ = 13.3 Hz, 3 H, CH$_3$), 7.19–7.30 (m, 6 H, H-*m*,*p*), 7.69–7.79 (m, 4 H, H-*o*) ppm. $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 21.4 (d, $^1J_{P,C}$ = 60.1 Hz, CH$_3$), 128.7 (d, $^3J_{P,C}$ = 12.1 Hz, C-*m*), 131.2 (d, $^2J_{P,C}$ = 10.6 Hz, C-*o*), 131.3 (d, $^4J_{P,C}$ = 2.7 Hz, C-*p*), 135.7 (d, $^1J_{P,C}$ = 81.2 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 35.8 ppm (s).

SePPh$_2$CH$_3$ (14): ^1H NMR (thf, 250.13 MHz): δ = 2.24 (d, $^2J_{P,H}$ = 13.6 Hz, 3 H, CH$_3$), 7.21–7.28 (m, 6 H, H-*m*,*p*), 7.71–7.79 (m, 4 H, H-*o*) ppm. $^{13}C\{^1H\}$ NMR (thf, 62.90 MHz): δ = 21.9 (d, $^1J_{P,C}$ = 53.3 Hz, CH$_3$), 128.7 (d, $^3J_{P,C}$ = 12.1 Hz, C-*m*), 131.4 (d, $^4J_{P,C}$ = 2.9 Hz, C-*p*), 131.6 (d, $^2J_{P,C}$ = 10.8 Hz, C-*o*), 134.4 (d, $^1J_{P,C}$ = 73.1 Hz, C-*i*) ppm. $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 24.3 ppm (s, $^1J_{PSe}$ = 744 Hz). ^{77}Se NMR (thf, 76.31 MHz): δ = –305.7 ppm (d, $^1J_{P,Se}$ = 744 Hz).

TePPh$_2$CH$_3$ (15): $^{31}P\{^1H\}$ NMR (thf, 161.98 MHz): δ = 25.6 ppm (s). $^{125}Te\{^1H\}$ NMR (thf, 126.19 MHz): δ = –554.5 ppm (s).

X-ray Structural Characterisation: Data collections were performed on a Stoe IPDS-II two-circle diffractometer with graphite-monochromated Mo-K_α radiation (see Tables 4 and 5). Empirical absorption corrections were performed with the MULABS option[41] in the program PLATON.[42] Equivalent reflections were averaged. The structures were solved by direct methods[43] and refined with full-matrix least-squares on F^2 using the program SHELXL-97.[44] Hydrogen atoms bonded to carbon and boron were placed at ideal positions and refined with fixed isotropic displacement parameters using a riding model.

CCDC-616914 (for **1**[c]), -616915 (for **2**[c]), -616916 (for **3**[c]), -616917 (for **4**[c]), -616918 (for **5**[c]), -616919 (for **6**[c]), -616920 (for

Table 4. Crystallographic data for compounds **1**[c]–**6**[c].

	1[c]	**2**[c]	**3**[c]	**4**[c]	**5**[c]	**6**[c]
Formula	$C_{24}H_{37}BKO_6P$	$C_{24}H_{37}BKO_7P$	$C_{24}H_{37}BKO_6PS$	$C_{24}H_{37}BKO_6PSe$	$C_{24}H_{37}BKO_6PTe$	$C_{20}H_{45}BKO_6P$
FW	502.42	518.42	534.48	581.38	630.02	462.44
Colour, shape	yellow, plate	colourless, block	colourless, block	colourless, block	pale brown, block	colourless, block
Temp. [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.3360(11)	10.5434(7)	8.5124(13)	9.1832(6)	9.2459(5)	9.1609(17)
b [Å]	10.3261(15)	14.2860(9)	30.376(4)	10.7869(7)	10.9071(6)	16.320(3)
c [Å]	28.178(3)	18.4297(11)	10.6730(17)	14.9362(10)	14.9509(9)	18.428(4)
α [°]	90	90	90	74.526(5)	74.104(5)	88.381(15)
β [°]	90	100.287(5)	99.230(13)	81.993(6)	83.045(5)	81.078(15)
γ [°]	90	90	90	86.034(5)	84.802(5)	86.627(15)
V [Å^3]	2716.5(6)	2731.3(3)	2724.0(7)	1411.23(16)	1436.81(14)	2716.5(9)
Z	4	4	4	2	2	4
$D_{calcd.}$ [g cm^{-3}]	1.228	1.261	1.303	1.368	1.456	1.131
F(000)	1072	1104	1136	604	640	1008
μ [mm^{-1}]	0.289	0.292	0.366	1.569	1.270	0.283
Cryst. size [mm]	0.34 × 0.12 × 0.03	0.46 × 0.35 × 0.30	0.50 × 0.41 × 0.32	0.39 × 0.34 × 0.22	0.29 × 0.16 × 0.09	0.36 × 0.33 × 0.28
Reflections collected	19217	39345	37292	40557	54151	19270
Indep. reflns. (R_{int})	4911 (0.1098)	5646 (0.0567)	5450 (0.1267)	7317 (0.0556)	5940 (0.0610)	9619 (0.0896)
Data/restraints/params.	4911/0/299	5646/0/307	5450/0/308	7317/6/326	5940/0/317	9619/0/526
GOOF on F^2	0.884	0.969	1.101	1.023	0.955	1.146
R_1, wR_2 [$I > 2\sigma(I)$]	0.0586, 0.1148	0.0302, 0.0730	0.1773, 0.3039	0.033, 0.082	0.0195, 0.0435	0.1186, 0.3066
R_1, wR_2 (all data)	0.1020, 0.1304	0.0435, 0.0764	0.2006, 0.3155	0.0423, 0.0857	0.0259, 0.0468	0.1595, 0.3498
Largest diff. peak and hole [e Å^{-3}]	0.717 and –0.211	0.370 and –0.251	0.507 and –0.424	0.379 and –0.410	0.374 and –0.330	0.787 and –0.558

Table 5. Crystallographic data for compounds **7**[c]–**10**[c] and **12**.

	7[c]	**8**[c]	**9**[c]	**10**[c]	**12**
Formula	$C_{20}H_{45}BKO_7P$	$C_{20}H_{45}BKO_6PS$	$C_{20}H_{45}BKO_6PSe$	$C_{20}H_{45}BKO_6PTe$	$C_{13}H_{13}OP$
FW	478.44	494.50	541.40	590.04	216.2
Colour, shape	colourless, block	colourless, block	colourless, rod	yellow, block	colourless, plate
Temp. [K]	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	9.6648(13)	9.4050(7)	9.3016(8)	9.8710(7)	8.6344(8)
b [Å]	15.4313(16)	14.7442(8)	14.8982(10)	14.8400(9)	24.2057(18)
c [Å]	18.745(3)	19.9463(12)	20.0229(17)	19.1333(14)	5.6957(6)
α [°]	90	90	90	90	90
β [°]	100.420(11)	98.900(5)	97.485(7)	92.265(6)	108.067(7)
γ [°]	90	90	90	90	90
V [Å^3]	2749.5(6)	2732.6(3)	2751.1(4)	2800.6(3)	1131.72(18)
Z	4	4	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.156	1.202	1.307	1.399	1.269
F(000)	1040	1072	1144	1216	456
μ [mm^{-1}]	0.284	0.359	1.604	1.297	0.212
Cryst. size [mm]	0.38 × 0.22 × 0.20	0.49 × 0.44 × 0.38	0.38 × 0.24 × 0.22	0.43 × 0.35 × 0.28	0.2 × 0.14 × 0.04
Reflections collected	29877	36838	32382	37620	9906
Indep. reflns. (R_{int})	5204 (0.0913)	5498 (0.0698)	5213 (0.0936)	5609 (0.0450)	1994 (0.0380)
Data/restraints/params.	5204/0/272	5498/0/272	5213/0/272	5609/0/272	1994/46/150
GOOF on F^2	0.785	1.036	0.860	0.866	1.033
R_1, wR_2 [$I > 2\sigma(I)$]	0.0374, 0.069	0.0369, 0.1059	0.0415, 0.0908	0.0197, 0.0419	0.0575, 0.1413
R_1, wR_2 (all data)	0.0845, 0.0776	0.0444, 0.1089	0.0718, 0.0979	0.0282, 0.0428	0.0642, 0.1457
Largest diff. peak and hole [e Å^{-3}]	0.394 and –0.289	0.305 and –0.580	0.569 and –0.720	0.493 and –0.344	0.821 and –0.497

7[c]), -616921 (for **8**[c]), -616922 (for **9**[c]), -616923 (for **10**[c]) and -616924 (for **12**) 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.

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