

# Trivinylphosphineborane (CH<sub>2</sub>=CH)<sub>3</sub>PBH<sub>3</sub> and related compounds

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In an investigation of the vinyl-activation in trivinylphosphine by acceptor molecules the 1 : 1 addition compounds with BH<sub>3</sub>, BCl<sub>3</sub>, BBr<sub>3</sub>, and BI<sub>3</sub> have been prepared. The reaction of Vi<sub>3</sub>P with BF<sub>3</sub> led to polymerization of the phosphine and its adduct. While the complexes (Vi<sub>3</sub>P)BX<sub>3</sub> with X = Cl, Br and I are air-stable colorless crystalline solids, (Vi<sub>3</sub>P)BH<sub>3</sub> is a colorless, distillable liquid. The NMR spectra show little variation in the chemical shifts and coupling constants of the nuclei of the vinyl groups with the nature of the halogen, but there are large differences as compared to the borane complex (X = H). The crystal structures of the three boron trihalide complexes are also very similar. The components Vi<sub>3</sub>P and BX<sub>3</sub> have a staggered conformation and the vinyl groups are in an all-*trans* propeller orientation. The variations in the bond distances and angles are very small and do not indicate major trends within the series. As shown by the successful preparation and structure elucidation of the reference compound (Et<sub>3</sub>P)BF<sub>3</sub>, the instability of (Vi<sub>3</sub>P)BF<sub>3</sub> is not due to an intrinsically low affinity of BF<sub>3</sub> to tertiary phosphines or a steric effect of the phosphine. (Et<sub>3</sub>P)BF<sub>3</sub> has an exceedingly long P–B donor–acceptor bond. It appears that BF<sub>3</sub> forms a weak complex, but is most effective in activating the vinyl groups for polymerization. In (Vi<sub>3</sub>P)BH<sub>3</sub> the three vinyl groups and the three B–H function would match for an intermolecular triple-hydroboration to give a three-dimensional polymer with C–C and P–B structural units, but neither of the two functionalities appears to be sufficiently activated to accomplish this reaction.

## Introduction

Trivinylphosphine<sup>1</sup> was prepared for the first time in 1957 but ever since it has been studied much less than the plethora of other tertiary phosphines which are well established as substrates, synthons and ligands in organic and coordination chemistry,<sup>2–8</sup> respectively. Until recently,<sup>9</sup> there was not only a deficit in efficient preparative methods for Vi<sub>3</sub>P, the compound also showed surprising non-standard behaviour even in simple quaternization or other reactions. It appeared that generation of a phosphonium center by addition of halogen, chalcogen, alkyl halides or acceptor molecules can cause a pronounced activation of the adjacent vinyl groups leading to complex side-reactions.<sup>9</sup> There are also scattered reports in the literature of a similar reaction behaviour of other vinylphosphines and their corresponding vinylphosphonium salts,<sup>5</sup> but very often the reactions have not been followed any further because of the puzzling results. The abnormal reaction pathways suggested that there is a delicate balance between various modes of substitution and addition which depends very strongly on the nature of the substituents and the oxidation or quaternization reagents.

There is also a paucity of data for simple adducts or complexes of trivinylphosphine with main group or transition metal acceptor components<sup>1,10–15</sup> which could show more clearly the influence of the complexation on the structure and bonding of the Vi<sub>3</sub>P component. In the present study we therefore investigated a series of simple boron hydride and halide adducts of the type (Vi<sub>3</sub>P)BX<sub>3</sub> with X = H, F, Cl, Br, and I. (Vi<sub>3</sub>P)BH<sub>3</sub> was obtained previously but not fully characterized.<sup>16</sup> This compound was of particular interest because it offered an ideal combination of three B–H and three –CH=CH<sub>2</sub> functions in the same molecule. It could therefore be expected to be a precursor for a three-dimensional network of phosphine–borane units (≡P–B≡) bridged by ethylidene links (–CH<sub>2</sub>–CH<sub>2</sub>–) generated in an exhaustive intermolecular hydroboration.

Of the four boron trihalides only BF<sub>3</sub> failed to give a stable adduct with trivinylphosphine, Vi<sub>3</sub>P. Therefore the corresponding trialkylphosphine complex, (Et<sub>3</sub>P)BF<sub>3</sub>, was also included in this study for comparison. Recently<sup>9</sup> we have also revisited the complex quaternization and oxidation reactions of Vi<sub>3</sub>P and Vi<sub>3</sub>As.

Adducts of boron halides BX<sub>3</sub> with phosphine PH<sub>3</sub> and primary, secondary and tertiary organophosphines PH<sub>n</sub>R<sub>3–n</sub> were studied extensively in the past.<sup>17–23</sup> This work has shown quite consistently that BF<sub>3</sub> forms the least stable 1 : 1 adducts. The set of trimethylphosphine complexes is a representative example in case: While the adducts with BCl<sub>3</sub>, BBr<sub>3</sub> and BI<sub>3</sub> could be crystallized and their structures determined, the BF<sub>3</sub> adduct was found to undergo rapid dissociation into its components on attempted crystallization.<sup>24–42</sup> It is therefore the more noteworthy that in the present work crystallization of the homologous (Et<sub>3</sub>P)BF<sub>3</sub> was successful.

## Preparative results

Trivinylphosphine-borane is readily obtained in good yield from equimolar quantities of the phosphine and dimethylsulfide-borane in toluene in the temperature regime from –40 to +20 °C. The product is a colourless, distillable liquid (bp 38 °C/0.9 mbar), but no single crystals could be grown from solutions or from the melt. The compound is stable at room temperature and is not sensitive to air and moisture.



This stability of a phosphine-borane is not unexpected. Most 1 : 1-adducts of tertiary phosphines with borane are known to be generally surprisingly robust.<sup>43–50</sup> Some representative examples are even resistant to strong oxidizing acid (sulfuric acid, nitric acid). The almost inert character of *e.g.* (Et<sub>3</sub>P)BH<sub>3</sub> or (Ph<sub>3</sub>P)BH<sub>3</sub> has been explained by a reduction of the polarity of the B–H bonds in BH<sub>3</sub>, or even their umpolung from (+)B–H(–) to (–)B–H(+), upon addition of the PR<sub>3</sub> donor with its σ-donor/π-acceptor/hyperconjugative properties.

For (Vi<sub>3</sub>P)BH<sub>3</sub> it is surprising, however, that the BH<sub>3</sub>-addition to Vi<sub>3</sub>P does not lead to an activation of the vinyl groups which is sufficient to induce either hydroboration or nucleophilic attack of phosphine as observed in other quaternization reactions.<sup>9</sup>

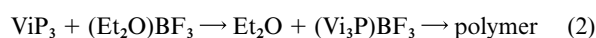
This activation is observed, however, in the reaction of Vi<sub>3</sub>P with (Et<sub>2</sub>O)BF<sub>3</sub> in hexane even at –50 °C. A colourless precipitate is formed immediately which cannot be redissolved in any

**Table 1** NMR data of (Vi<sub>3</sub>P)BH<sub>3</sub>, (Vi<sub>3</sub>P)BCl<sub>3</sub>, (Vi<sub>3</sub>P)BBr<sub>3</sub>, (Vi<sub>3</sub>P)BI<sub>3</sub> and (Et<sub>3</sub>P)BF<sub>3</sub>

	<sup>31</sup> P{ <sup>1</sup> H} [ppm] ( <i>J</i> (BP)/Hz)	<sup>11</sup> B{ <sup>1</sup> H} [ppm]	<sup>13</sup> C{ <sup>1</sup> H} [ppm] ( <i>J</i> (CP)/Hz)		<sup>1</sup> H [ppm] C1–H	C2–H
			C1	C2		
(Vi <sub>3</sub> P)BH <sub>3</sub> <sup>a</sup>	8.56 (51.7)	43.59	127.9 (101.47)	133.6 (4.67)	5.51–5.97; 1.34 (BH <sub>3</sub> )	
(Vi <sub>3</sub> P)BCl <sub>3</sub> <sup>b</sup>	–9.73 (159.5)	1.99	119.1 (64.36)	140.6 (—)	6.2–6.7	
(Vi <sub>3</sub> P)BBr <sub>3</sub>	–10.83 (155.6) <sup>b</sup>	–16.40 <sup>b</sup>	119.5 (67.99)	140.7 (—) <sup>a</sup>	6.39 <sup>a</sup>	6.24, 6.62
(Vi <sub>3</sub> P)BI <sub>3</sub>	–15.61 (134.3) <sup>b</sup>	–74.33 <sup>b</sup>	120.6 (72.15)	140.6 (—) <sup>a</sup>	6.4–6.6 <sup>a</sup>	6.28, 6.68
(Et <sub>3</sub> P)BF <sub>3</sub> <sup>b</sup>	–7.64 (168.6)	0.89	9.9 (48.27)	6.7 (5.71)	2.27	1.29

<sup>a</sup> C<sub>6</sub>D<sub>6</sub>; <sup>b</sup> CD<sub>2</sub>Cl<sub>2</sub>.

common organic solvent. After washing with hexane and drying in a vacuum, no soluble components can be extracted from this product with dichloromethane. These properties suggest a polymeric structure which arises from nucleophilic attack of the phosphine at one of the vinyl groups of the primary adduct (Vi<sub>3</sub>P)BF<sub>3</sub>. This side reaction competes favourably with the simple 1 : 1-adduct formation and affords a branched-chain polymer. The elemental analysis data of the products of different runs of this reaction varied significantly indicating only partial incorporation of BF<sub>3</sub> into the polymer.



By contrast, all reactions of Vi<sub>3</sub>P with BCl<sub>3</sub>, BBr<sub>3</sub> and BI<sub>3</sub> under similar conditions (in hexane at –50 °C) gave stable crystalline 1 : 1-adducts in good yields [eqn. (3)].



All three adducts can be crystallized from dichloromethane at –78 °C, and the BCl<sub>3</sub>-complex can be sublimed in a vacuum without decomposition. The compounds can be kept in carefully sealed vessels for long periods of time. The composition has been confirmed by elemental analysis and by mass spectrometry.

In order to learn if the unexpected low stability of the (Vi<sub>3</sub>P)BF<sub>3</sub> complex is based on an intrinsically low affinity of BF<sub>3</sub> towards tertiary phosphines in general, or on steric effects of the particular phosphine, we included the complex (Et<sub>3</sub>P)BF<sub>3</sub> into the preparative program. It could be demonstrated that this complex is readily obtained from its components and is perfectly stable towards dissociation at room temperature.



### NMR-spectroscopic studies

The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR data of the compounds (Vi<sub>3</sub>P)BX<sub>3</sub> with X = H, Cl, Br, I, and of (Et<sub>3</sub>P)BF<sub>3</sub> are summarized in Table 1. A comparison of the parameters for the newly formed dative P–B bonds is of particular interest.

The <sup>31</sup>P resonances cover a shift range from 8.56 ppm (in benzene at 20 °C) for X = H to –9.7, –10.8 and –15.6 ppm (in dichloromethane at 20 °C) for X = Cl, Br and I, respectively. Only the BH<sub>3</sub>-adduct shows the usual large down-field shift upon adduct formation [from δP = –19.0 ppm for free Vi<sub>3</sub>P], while this shift is much less as the atomic number of the halogen of the BX<sub>3</sub> acceptor is increased. This phenomenon has already been observed in other (R<sub>3</sub>P)BX<sub>3</sub> complexes and related to bond increments of the electron-rich BX<sub>3</sub> molecules which are different from those of BH<sub>3</sub>. Similar results were also obtained for aluminium, gallium and indium trihalide complexes.<sup>51</sup>

The <sup>11</sup>B resonances cover a broad range of more than 100 ppm from 43.6 ppm for X = H to 2.0, –16.4 and –74.3 ppm for X = Cl, Br and I, respectively. These shifts are of course influenced even more by the B–X bond increments. The

<sup>1</sup>J(<sup>31</sup>P–<sup>11</sup>B) coupling constant in (Vi<sub>3</sub>P)BX<sub>3</sub> is found to be 52 Hz for X = H, but as much as 159.5, 155.6 and 134.3 Hz for X = Cl, Br, I, respectively. These values suggest profound differences in P–B bonding of the BH<sub>3</sub> and BX<sub>3</sub> adducts as related mainly to gradation of electronegativities of the elements involved.<sup>11</sup> High electronegativity of X leads to an increase of p-character of the orbitals of the central boron atom employed in bonding of X and consequently high s-character of the remaining bond to boron (P–B). Following the Fermi contact principle, the least electronegative substituent (H) thus gives rise to the smallest J(P–B) coupling constant.

The <sup>1</sup>J(<sup>31</sup>P–<sup>11</sup>B) coupling constants are clearly correlated with the <sup>1</sup>J(<sup>31</sup>P–<sup>13</sup>C) coupling constants as reflected by the values 101.5, 64.4, 68.0, and 72.2 Hz for X = H, Cl, Br and I, respectively. P–C coupling is largest for the hydride, but smaller (but progressively larger as the atomic number of halide increases) for the three halides, while for P–B coupling the opposite is true (smallest for the hydride and higher, but progressively smaller, for the halides). The above electronegativity/hybridization reasoning (“Bent’s rule”) requires this correlation.

The chemical shift δ(<sup>13</sup>C) for carbon atoms C1 is high for X = H (127.9 ppm) and consistently smaller for X = Cl, Br, I (119.1, 119.5 and 120.6 ppm). The reference value for free Vi<sub>3</sub>P is δC 136.7 ppm. The upfield shifts upon complexation are mainly influenced by the rehybridization of the phosphorus atom upon quaternization, but may also reflect contributions from resonance forms [(+)CH<sub>2</sub>–CH=PR<sub>2</sub>BX<sub>3</sub>(–)]. For carbon atoms C2 the values are almost identical for the three halides (140.6 ± 0.1 ppm) and smaller for X = H (133.6 ppm). This variation indicates a significant deshielding of carbon atoms C2 as compared to the free Vi<sub>3</sub>P [δ(C2) 127.2 ppm] which makes them—also according to the above resonance form—more susceptible for nucleophilic attack. From electronegativity considerations, BF<sub>3</sub> with the most electronegative halogen substituent will lead to the strongest deshielding of carbon atoms C2 (δ ca. 145 ppm) such that polymerization becomes the dominant reaction initiated by BF<sub>3</sub> coordination.

Finally it should be noted that Vi<sub>3</sub>P and Et<sub>3</sub>P have almost the same chemical shift, δP = –19 and –20 ppm, respectively. In the complex (Et<sub>3</sub>P)BF<sub>3</sub> the signal of the ligand is shifted to +7.6 ppm.

### Structural studies

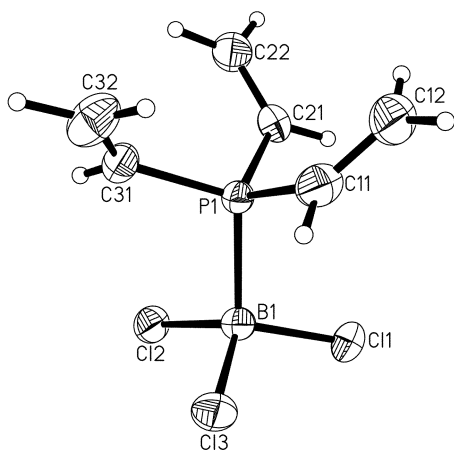
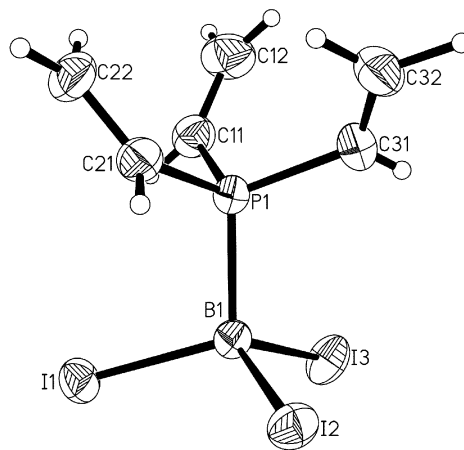
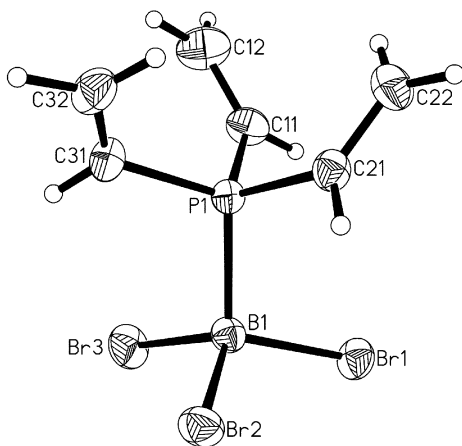
Solvent-free single crystals could be grown (from dichloromethane at –78 °C) of all three boron trihalide complexes. Crystal and structure solution data are compiled in Table 2 (see Experimental). (Vi<sub>3</sub>P)BH<sub>3</sub> is a volatile liquid and has a low melting point. Attempted crystal growth from the melt in a capillary on the diffractometer was not successful.

The crystals of the three boron trihalide complexes (X = Cl, Br, I) are not isomorphous [Cl: orthorhombic, *Pna*2<sub>1</sub>, *Z* = 4 (racemic twin). Br: monoclinic, *P2<sub>1</sub>/n*, *Z* = 4. I: monoclinic, *P2<sub>1</sub>/c*, *Z* = 4], but the configuration and conformation of the molecules are very similar.

In the crystals none of the molecules has any crystallographically imposed symmetry, but the geometry approaches

**Table 2** Crystal data, data collection, and structure refinement of  $(\text{Vi}_3\text{P})\text{BCl}_3$ ,  $(\text{Vi}_3\text{P})\text{BBr}_3$ ,  $(\text{Vi}_3\text{P})\text{BI}_3$  and  $(\text{Et}_3\text{P})\text{BF}_3$ 

	$(\text{Vi}_3\text{P})\text{BCl}_3$	$(\text{Vi}_3\text{P})\text{BBr}_3$	$(\text{Vi}_3\text{P})\text{BI}_3$	$(\text{Et}_3\text{P})\text{BF}_3$
Empirical formula	$\text{C}_6\text{H}_9\text{BCl}_3\text{P}$	$\text{C}_6\text{H}_9\text{BBr}_3\text{P}$	$\text{C}_6\text{H}_9\text{BI}_3\text{P}$	$\text{C}_6\text{H}_{15}\text{BF}_3\text{P}$
<i>M</i>	229.26	362.64	503.61	185.96
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/n$	$P2_12_12_1$
<i>a</i> /Å	13.6690(3)	6.95430(10)	7.2500(1)	6.42400(10)
<i>b</i> /Å	6.40700(10)	11.3363(2)	11.8070(2)	9.2453(2)
<i>c</i> /Å	12.5050(3)	14.5709(2)	15.1560(3)	16.2097(3)
$\beta$ /°	90	93.1093(10)	94.6730(8)	90
<i>U</i> /Å <sup>3</sup>	1095.15(4)	1147.02(3)	1293.05(4)	962.72(3)
<i>Z</i>	4	4	4	4
<i>T</i> /K	143	143	143	143
Reflections measured	34487	45210	33405	30675
Reflections unique	2407 [ $R_{\text{int}} = 0.046$ ]	3930 [ $R_{\text{int}} = 0.050$ ]	3029 [ $R_{\text{int}} = 0.0381$ ]	2207 [ $R_{\text{int}} = 0.025$ ]
Refined parameters/restraints	137/1	136/0	136/0	161/0
<i>R</i> 1 [ $I \geq 2\sigma(I)$ ]	0.0283	0.0304	0.0278	0.0297
<i>wR</i> 2	0.0626	0.0680	0.0706	0.0797

**Fig. 1** Molecular structure of  $(\text{Vi}_3\text{P})\text{BCl}_3$ . ORTEP,<sup>55</sup> 50% probability ellipsoids. Selected bond lengths [Å], angles and torsion angles [°]: B1–P1 1.970(2), P1–C11 1.786(2), P1–C21 1.786(2), P1–C31 1.781(2), B1–C11 1.841(3), B1–C12 1.847(2), B1–C13 1.845(2); C11–P1–C21 108.8(1), C11–P1–B1 109.9(1), C11–B1–C12 112.5(1), C11–B1–P1 107.5(1), C11–P1–B1–C11 68.1(2), C21–P1–B1–C11 52.0(1), C31–P1–B1–C11 171.9(1), B1–P1–C11–C12 125.6(2), B1–P1–C21–C22 131.6(2), B1–P1–C31–C32 128.9(2).**Fig. 3** Molecular structure of  $(\text{Vi}_3\text{P})\text{BI}_3$ . ORTEP, 50% probability ellipsoids. Selected bond lengths [Å], angles and torsion angles [°]: B1–P1 1.944(4), P1–C11 1.787(5), P1–C21 1.787(4), P1–C31 1.798(5), B1–I1 2.228(4), B1–I2 2.226(5), B1–I3 2.232(4); C11–P1–C21 108.4(2), C11–P1–B1 110.9(2), I1–B1–I2 112.5(2), P1–B1–I1 106.7(2), I1–P1–B1–C11 60.9(2), C21–P1–B1–I1 58.8(3), C31–P1–B1–I1 178.0(2), B1–P1–C11–C12 144.1(4), B1–P1–C21–C22 137.8(4), B1–P1–C31–C32 136.6(4).**Fig. 2** Molecular structure of  $(\text{Vi}_3\text{P})\text{BBr}_3$ . ORTEP, 50% probability ellipsoids. Selected bond lengths [Å], angles and torsion angles [°]: B1–P1 1.952(2), P1–C11 1.789(2), P1–C21 1.792(2), P1–C31 1.795(2), B1–Br1 2.004(2), B1–Br2 2.009(2), B1–Br3 2.005(2); C11–P1–C21 108.3(1), C11–P1–B1 110.6(1), Br1–B1–Br2 111.9(1), P1–B1–Br1 106.8(1), C11–P1–B1–Br1 60.7(1), Br1–P1–B1–C21 58.7(1), Br1–P1–B1–C31 178.5(1), B1–P1–C11–C12 140.5(2), B1–P1–C21–C22 137.8(2), B1–P1–C31–C32 139.6(2).

quite closely the requirements of a threefold axis (Figs. 1–3). The  $\text{BX}_3$  and  $\text{Vi}_3\text{P}$  parts are staggered relative to each other. Thus *e.g.* in  $(\text{Vi}_3\text{P})\text{BCl}_3$  the plane C11–B1–P1 is approximately

bisecting the angle C11–P1–C21 with torsional angles C11–B1–P1–C11 68°, C11–B1–P1–C21 52° and C11–B1–P1–C31 172°.

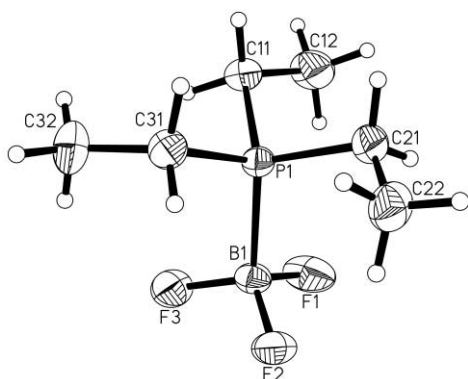
The three vinyl groups have a propeller-type conformation with an all-*anti* orientation and very similar torsional angles B–P–C–C larger than 90°. Typically these torsional angles in  $(\text{Vi}_3\text{P})\text{BCl}_3$  are 125.6, 131.6 and 128.9° with the same rotatory direction. Because of this point group  $C_3$  symmetry the molecules are chiral and appear as left- and right-handed propellers. Both enantiomers are present in the crystals either in racemic twins or related by space group symmetry.

It should be noted that the free  $\text{Vi}_3\text{P}$  ligand is predicted to have the vinyl groups rotated into an all-*cis* conformation (point group  $C_3$ ), *i.e.* with the vinyl groups oriented towards the lone-pair of electrons at the phosphorus atom. This configuration is changed to mixed *cis/trans* conformations as the phosphorus atom is either quaternized (Me), oxidized (O, S, Se) or coordinated ( $\text{AuCl}$ ),<sup>9</sup> but the all-*trans* orientation is required only with the bulky  $\text{BX}_3$  acceptors as shown in this work.

The structural data that could be related to the donor-acceptor strengths in the three adducts show very small variations. It is surprising to find that all nine P–C distances of the three  $\text{Vi}_3\text{P}$  ligands are within the narrow range between 1.781(2) and 1.798(5)° and all nine C–P–C angles between 107.7(2) and 108.84(12)°, with the differences barely exceeding the standard deviation limits. It is only the P–B bond length which shows a more significant regression on going from X = Cl [1.970(2) Å] to Br [1.952(2) Å] and I [1.944(4) Å]. The P–B bond thus is

shortest for the iodide and longest for the chloride. It is unlikely, however, that this regression of the P–B bond length alone is a reliable indicator for the donor–acceptor interaction and its activating influence on the distant vinyl groups. The C=C bond lengths of the three compounds are all equal within the limits of experimental standard deviations.

The reference compound (Et<sub>3</sub>P)BF<sub>3</sub> crystallizes in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> with *Z* = 4 formula units in the unit cell. The BF<sub>3</sub> and Et<sub>3</sub>P components are in a staggered conformation similar to the arrangement in the three (Vi<sub>3</sub>P)BX<sub>3</sub> adducts (above). Like in these compounds the overall symmetry approaches quite closely the point group C<sub>3</sub>, but the three ethyl groups have B–P–C–C torsional angles much *smaller* than 90° [B1–P1–C11–C12 –65.91(13), B1–P1–C21–C22 –71.13(13), B1–P1–C31–C32 –66.93(13)] (Fig. 4). This means that the ethyl groups are rotated *towards* the BF<sub>3</sub> unit, while in the Vi<sub>3</sub>PBX<sub>3</sub> molecules the vinyl groups are rotated *away* from the BX<sub>3</sub> units. This conformation may be due to the reduced steric bulk of the BF<sub>3</sub> unit as compared to BX<sub>3</sub> units with the larger halogen atoms (X = Cl, Br, I). All C–P–C, F–B–F, F–B–P, and B–P–C angles, as well as all P–C, C–C and B–F distances in (Et<sub>3</sub>P)BF<sub>3</sub> are found to be normal and indicate a standard geometry of an ethane-type molecule.



**Fig. 4** Molecular structure of (Et<sub>3</sub>P)BF<sub>3</sub>. ORTEP, 50% probability ellipsoids. Selected bond lengths [Å], angles and torsion angles [°]: B1–P1 2.028(1), P1–C11 1.816(1), P1–C21 1.820(1), P1–C31 1.814(1), B1–F1 1.378(2), B1–F2 1.384(2), B1–F3 1.383(2); C11–P1–C21 107.37(7), C11–P1–B1 112.32(6), F1–B1–F2 110.5(1), P1–B1–F1 108.53(9), C11–P1–B1–F1 54.2(1), F1–P1–B1–C21 66.2(1), C31–P1–B1–F1 174.7(1), C12–C11–P1–B1 65.9(1), C22–C21–P1–B1 71.1(1), C32–C31–P1–B1 66.9(1).

However, there is yet another more conspicuous difference between the (Vi<sub>3</sub>P)BX<sub>3</sub> molecules and (Et<sub>3</sub>P)BF<sub>3</sub>: In the latter the P–B bond is *very significantly longer* at 2.0280(14) Å, which suggests a weak donor–acceptor interaction. [For (Vi<sub>3</sub>P)BCl<sub>3</sub> the P–B bond length is 1.970(2) Å!]. Assuming that the P–B bond length in (Vi<sub>3</sub>P)BF<sub>3</sub> (the only compound which could not be isolated) would be similar, this could mean that the BF<sub>3</sub>-coordination is sufficient to activate the vinyl groups for polymerization, but not strong enough to block the phosphine function irreversibly.

## Experimental

### General procedures

All chemicals used as starting materials were commercially available, except Vi<sub>3</sub>P and BI<sub>3</sub> which were prepared according to the literature.<sup>9,52</sup>

Reactions were carried out under an atmosphere of purified nitrogen. All solvents were distilled from an appropriate drying agent and stored above molecular sieves (4 Å) and under nitrogen. Mass spectra were recorded on a Finnigan MAT 90 spectrometer using CI as an ionization method. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270

spectrometers. Chemical shifts are reported in  $\delta$  values relative to the residual solvent resonances (<sup>1</sup>H, <sup>13</sup>C). <sup>31</sup>P-, <sup>11</sup>B- and <sup>19</sup>F{<sup>1</sup>H} NMR spectra are referenced to external aqueous H<sub>3</sub>PO<sub>4</sub> (85%), BF<sub>3</sub>·OEt<sub>2</sub> and CFCl<sub>3</sub>, respectively. The single-crystal X-ray diffraction measurements were performed at –130 °C on a Nonius DIP 2020 diffractometer using graphite monochromated Mo-K $\alpha$  radiation.

**Preparation of trivinylphosphine-borane.** To a solution of Me<sub>2</sub>SBH<sub>3</sub> in toluene (2.0 M, 2 mL, 4.0 mmol) was added Vi<sub>3</sub>P (0.5 g, 4.5 mmol) at –40 °C *via* a syringe. The reaction mixture was allowed to warm to room temperature and the solvent removed *in vacuo*. The product was isolated as a colorless liquid by distillation (38 °C, 0.9 mbar). Yield: 0.39 g (68%). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  8.56 (q, *J* = 51.7 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  43.59 (d, *J* = 53.00 Hz). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  133.62 (d, *J* = 4.67 Hz, C2), 127.9 (d, *J* = 101.47 Hz, C1). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  5.51–5.97 (ABCX, 9 H, Vi–H), 1.34 (dq, *J* = 98.47 and 15.09 Hz, 3 H, BH<sub>3</sub>).

**Preparation of trivinylphosphine-borontrichloride.** To a solution of trivinylphosphine (0.66 g, 5.9 mmol) in hexane (5 mL) was added a solution of BCl<sub>3</sub> (1 M in hexane, 5.0 mL, 5.0 mmol) in additional hexane (5 mL) at –50 °C *via* a syringe. A white precipitate was formed, which was filtered and purified *via* sublimation at 119 °C. Single crystals were obtained by cooling a solution in dichloromethane to –78 °C. Yield: 0.75 g (88%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  –9.73 (q, *J* = 159.53 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  1.99 (d, *J* = 162.62 Hz). <sup>13</sup>C{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  140.6 (s, C2), 119.1 (d, *J* = 64.36 Hz, C1). <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  6.2–6.7 (ABCX, 9 H, Vi–H). Elemental analysis calc. for C<sub>6</sub>H<sub>9</sub>PBCl<sub>3</sub> (229.26): C, 31.43; H, 3.96; P, 13.51; Cl, 46.39. Found: C, 31.53; H, 3.99; P, 13.33; Cl, 46.18%. MS (CI) *m/z*: 193.0 (42.0%) [M – Cl]<sup>+</sup>, 139.0 (3.5%) [M – 2Vi – Cl]<sup>+</sup>.

**Preparation of trivinylphosphine-borontribromide.** To a solution of trivinylphosphine (0.28 g, 2.5 mmol) in hexane (5 mL) was added a solution of BBr<sub>3</sub> (1 M in hexane, 2.5 mL, 2.5 mmol) in hexane (5 mL) at –50 °C *via* a syringe. A white precipitate was formed, which was filtered, washed with hexane (3 × 5 mL) and dried *in vacuo*. Single crystals were obtained by cooling a solution in dichloromethane to –78 °C. Yield: 0.13 g (14%). Mp 151 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  –10.83 (q, *J* = 155.57 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  –16.40 (d, *J* = 155.57 Hz). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  140.7 (s, C2), 119.5 (d, *J* = 67.99 Hz, C1). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  6.62 (ddd, *J* = 40.67, 11.25 and 1.82 Hz, 3 H, C2–H), 6.39 (ddd, *J* = 22.79, 18.48 and 11.25 Hz, 3 H, C1–H), 6.24 (ddd, *J* = 20.68, 18.48 and 1.82 Hz, 3 H, C2–H). Elemental analysis calc. for C<sub>6</sub>H<sub>9</sub>PBBBr<sub>3</sub> (362.54): C, 19.87; H, 2.50; P, 8.54; Br, 66.10. Found: C, 19.93; H, 2.55; P, 8.38; Br, 66.78%. MS (CI) *m/z*: 283.1 (36.8%) [M – Br]<sup>+</sup>, 170.9 (33.3%) [BBr<sub>2</sub>]<sup>+</sup>.

**Preparation of trivinylphosphine-borontriiodide.** To a solution of trivinylphosphine (0.40 g, 3.6 mmol) in hexane (5 mL) was added a solution of BI<sub>3</sub> (1.4 g, 3.7 mmol) in hexane (5 mL) at –50 °C *via* a dropping funnel. A white precipitate was formed, which was filtered, washed with hexane (3 × 5 mL) and dried *in vacuo*. Single crystals were obtained by cooling a solution in dichloromethane to –78 °C. Yield: 1.6 g (89%). Decomposition: 200 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  –15.61 (q, *J* = 134.33 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, rt):  $\delta$  –74.33 (d, *J* = 134.62 Hz). <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  140.6 (s, C2), 120.6 (d, *J* = 72.15 Hz, C1). <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, rt):  $\delta$  6.68 (ddd, *J* = 40.75, 11.95 and 1.19 Hz, 3 H, C2–H), 6.4–6.6 (ABCX, 3 H, C1–H), 6.28 (ddd, *J* = 20.56, 18.33 and 1.19 Hz, 3 H, C2–H). Elemental analysis calc. for C<sub>6</sub>H<sub>9</sub>PBI<sub>3</sub> (503.62): C, 14.31; H, 1.80; P, 6.15; I, 75.59. Found: C, 14.51; H, 1.95; P, 6.04; I, 74.55%. MS (CI) *m/z*: 377.3 (100%) [M – I]<sup>+</sup>, 265.0 (14.38%) [BI<sub>2</sub>]<sup>+</sup>, 127.9 (19.0%) [I]<sup>+</sup>.

**Preparation of triethylphosphine-borontrifluoride.** Borontrifluoride-etherate (0.5 mL, 4.2 mmol) was dispersed in hexane (5 mL) and cooled to  $-60\text{ }^{\circ}\text{C}$ . Triethylphosphine (0.5 g, 4.2 mmol), dissolved in hexane (5 mL), was slowly added *via* a syringe. A white precipitate was formed immediately. The reaction mixture was allowed to warm to room temperature and filtered. Crystals were obtained from dichloromethane/pentane at  $-36\text{ }^{\circ}\text{C}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , rt):  $\delta -7.64$  [qq,  $J(\text{PB}) = 168.60$  Hz,  $J(\text{PF}) = 215.01$  Hz].  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , rt):  $\delta 0.89$  [dq,  $J(\text{BP}) = 169.68$  Hz,  $J(\text{BF}) = 53.00$  Hz].  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , rt):  $\delta 9.9$  (d,  $J = 48.27$  Hz, C1), 6.7 (d,  $J = 5.71$  Hz, C2).  $^1\text{H}$  ( $\text{CD}_2\text{Cl}_2$ , rt):  $\delta 2.27$  (dq,  $J = 20.66$  and  $7.67$  Hz, 6 H, C1-H), 1.29 (dt,  $J = 20.29$  and  $7.67$  Hz, 9 H, C2-H).  $^{19}\text{F}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , rt):  $\delta -150.7$  (s). For further analytical data see references 17, 20 and 22.

### Crystal structure determination

Specimens of suitable quality and size of  $(\text{Vi}_3\text{P})\text{BCl}_3$ ,  $(\text{Vi}_3\text{P})\text{BBr}_3$ ,  $(\text{Vi}_3\text{P})\text{BI}_3$  and  $(\text{Et}_3\text{P})\text{BF}_3$  were mounted on the ends of quartz fibers in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K $\alpha$  radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on  $F^2$  (SHELXL-97).<sup>53</sup> The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were located and refined isotropically. Absorption corrections for  $(\text{Vi}_3\text{P})\text{BBr}_3$  and  $(\text{Vi}_3\text{P})\text{BI}_3$  were carried out using DELABS, as part of the PLATON suite of programs.<sup>54</sup> Further information on crystal data, data collection and structure refinement are summarized in Table 2.

CCDC reference numbers 197160–197163.

See <http://www.rsc.org/suppdata/dt/b2/b210991c/> for crystallographic data in CIF or other electronic format.

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