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Phosphane–boranes: synthesis, characterization and synthetic applications

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Abstract

The chemistry of borane (BH_3) complexes of tricoordinated phosphorus compounds is reviewed, including the preparation, coordination chemistry, reactivity and synthetic applications.

Keywords: Organophosphorus compounds; Borane; Phosphane–borane complexes

List of Abbreviations

o-An	*ortho*-anisyl
Ant	anthryl
Bn	benzyl
n-Bu	*n*-butyl
sec-Bu	*sec*-butyl
t-Bu	*tertiary*-butyl
DABCO	diazabicyclo[2.2.2.]octane
Et	ethyl
Men	menthyl
P.C.C.	pyridiniumchlorochromate or Corey's reagent
Ph	phenyl
i-Pr	*iso*-propyl
n-Pr	*n*-propyl
Py	pyridine
THF	tetrahydrofurane
TMEDA	tetramethylethylenediamine

1. Introduction

Phosphane–borane complexes, adducts of phosphanes and borane, have attracted a growing interest over the past four decades. The unexpected stability of trimethylphosphane–borane and its homologues has focused a great number of investigations, which have revealed the peculiar chemical properties of such compounds as well as the inherent P–B bond nature. Although some monographs in this area have already appeared [1,2], the aim of this review is to highlight the main features of borane adducts of tricoordinated phosphorus compounds in their synthesis, coordination chemistry and synthetic applications.

2. Synthesis of phosphane–borane complexes

2.1. From PR_3 and diborane

Although the first compound containing a P–B bond ($H_3P.BCl_3$) was described as early as 1890 by Besson [3], it was not until 1940 that the first fundamental study

on phosphane–boranes was reported [4]. Thus, the reaction of phosphane PH_3 and diborane B_2H_6 at low temperature led to the formation of $PH_3.BH_3$ as a white crystalline solid, which dissociates above -30 °C into diborane and phosphane. The same procedure was used to prepare $MePH_2.BH_3$, $Me_2PH.BH_3$ and $Me_3P.BH_3$ [5,6]. These adducts were found to be much more stable, easily handled compounds. This higher stability has been accounted for by the increased basic character of methyl phosphanes over PH_3. This hypothesis has been corroborated by the instability reported for $PF_3.BH_3$ which dissociates at room temperature [7], and by the fact that trifluoromethyl substituted phosphanes (known as weak bases) give elusive adducts [8].

This method thus allowed the further synthesis of several phosphane–borane complexes such as triphenylphosphane–borane [9], diphenylphosphane–borane [10], aminophosphane–boranes [11–14], phosphite–boranes [15–17], dialkyl(trimethylsilyl)phosphane–boranes [18], chlorodimethylphosphane–borane [19] and (difluoromethyl)phosphane–boranes [20]. Biphosphane–boranes $P_2H_4.BH_3$ [21,22], $BH_3.P_2H_4.BH_3$ [21,23] and $BH_3.Me_2PPMe_2.BH_3$ [24] have also been reported and characterized.

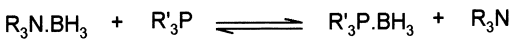
It should be pointed out that this method enables the synthesis of isotopically labeled compounds such as deuterioborane adducts [9,16,19,23] and $^{10}BH_3.P(C_6H_5)_3$ [9].

2.2. From PR_3 and borane complexes

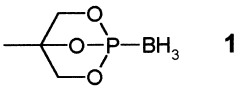
Although the method described above has been often used, it suffers from the hazards involved with the use of gaseous diborane. Borane–amine complexes provide a safer source of BH_3 and have been frequently employed. In this case, their reaction with a tricoordinated phosphorus compound is in equilibrium with the phosphane–borane and the free amine (Scheme 1).

This feature has led to different studies based on the synthetic point of view but also as a means to evaluate the relative Lewis base strengths of the phosphorus compounds by their ability to displace R_3N from its borane adduct. For example, Graham and Stone [25] have found that Me_3P displaces Me_3N in $Me_3N.BH_3$, the equilibrium being 80% in favor of the phosphane adduct. Similar results were obtained with $(Me_2N)_3P$ [12], whereas triisopropyl phosphite displaces Me_3N only to the extent of 53% [15]. On the other hand, the electron donor power of phosphorus trifluoride is much weaker and, as a consequence, Me_3N quantitatively displaces PF_3 from $PF_3.BH_3$ [7]. Similarly, the bicyclic phosphite complex **1** reacts quantitatively with one equivalent of trimethylamine to produce $Me_3N.BH_3$ and the free phosphite [16]. This was also interpreted through the weak donor ability of this cage phosphite, which is in sharp contrast with its acyclic counterparts (Scheme 2).

Thus, the reaction allows a classification of the basicity of tricoordinated phos-



Scheme 1.



1

Scheme 2.

phorus compounds vs trialkyl amines (or dialkyl amines [26]) whose influence in the distribution of the equilibrium has been rationalized on the basis of kinetic measurements [27].

From a synthetic point of view, this reaction necessitates a complete displacement of the equilibrium, which is effected by distilling off the amine from the reaction mixture [13,28]. An alternative procedure consists in the use of a sterically crowded amine such as $(i\text{-Pr})_2NEt$ which will release BH_3 more easily, as exemplified with the recent synthesis of 5′-P–borane substituted thymine monophosphate [29].

The increased commercial availability of other more labile borane complexes (BH_3.THF, $BH_3.SMe_2$,…) has led to their frequent use for the synthesis of phosphane–boranes such as $(PhO)_3P.BH_3$ [30], $Me_2PCl.BH_3$ [31–33], $Ph_2PCl.BH_3$ [34] and $(Et_2N)_2PCl.BH_3$ [35]. This is particularly useful in the case of $Me_3P.BH_3$, because the exchange reaction with borane–triethylamine cannot be used for its preparation since the liberated amine and trimethylphosphane are difficult to separate [36].

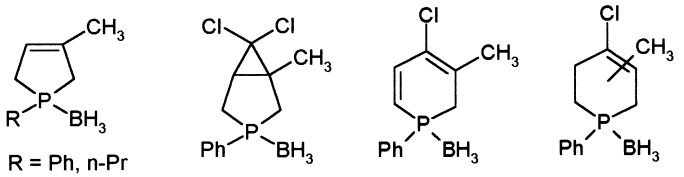
Keglevich et al. [37–40] have reported the preparation of adducts **2–5** by reaction of $BH_3.SMe_2$ with the corresponding free phosphanes which, in turn, were obtained from their oxides *via* reduction with trichlorosilane (Scheme 3).

The reaction of 3,4-dimethyl-1-phenylphosphole with $BH_3.SMe_2$ gives the corresponding adduct in 93% chemical yield [41].

Similarly, the borane adducts of phenylphosphane, methylphosphane [42] and dicyclohexylphosphane [43] have also been prepared recently.

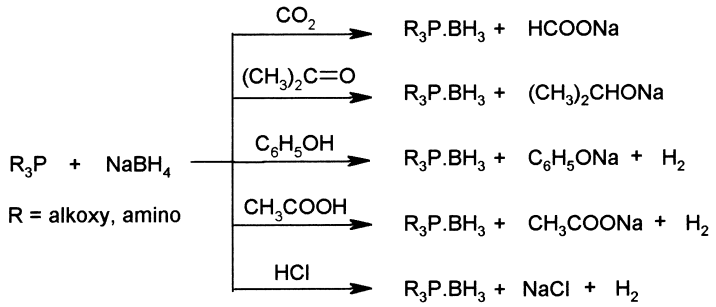
2.3. *From PR_3 and borohydrides*

Borohydrides can be considered as borane combined with a hydride, so BH_3 can be generated in situ to react further with the tricoordinated phosphorus compound. This was first described by Reetz et al. for the preparation of tris(dialkylamino)phosphane–boranes [12] and trialkylphosphite–boranes [15]. However, an additional reagent must be employed since borohydride alone cannot deliver BH_3. Several reagents can be used as depicted in the following (Scheme 4):



2 **3** **4** **5**

Scheme 3.



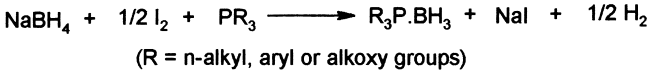
Scheme 4.

These additional reagents convert $NaBH_4$ into a species reactive to the phosphorus starting material. Trimethylphosphane–borane has also been obtained by this method [36]. Iodine was also effective as "additional reagent" (Scheme 5) [44].

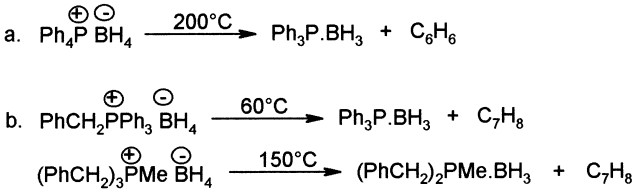
A related reaction relies on the thermal decomposition of quaternary phosphonium borohydrides which are obtained by an exchange reaction between quaternary phosphonium bromides and sodium borohydride. These salts are cleaved to yield the adducts (Scheme 6(a) [45] and Scheme 6(b) [17]).

This reaction has been limited to phosphonium borohydrides containing the labile phenyl or benzyl groups.

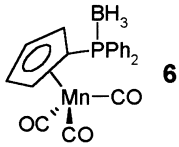
On heating bis(cymanthrenyldiphenylphosphane) copper(I) tetrahydroborate, cymanthrenyl-diphenylphosphane–borane **6** is obtained (Scheme 7) [46].



Scheme 5.



Scheme 6.



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Scheme 7.

2.4. By reduction of phosphanes precursors

The methods described above are not always easily accomplished since some phosphanes, particularly secondary and primary phosphanes, are very difficult to handle because of their corrosiveness, air sensitivity and toxicity. Furthermore, most of them are malodorous compounds. Therefore, a number of synthetic approaches have been devised from more easily handled starting materials. Thus, Wiberg and Nöth [47] prepared phenylphosphane–borane by reacting phenyldichlorophosphane and lithium borohydride in a molar ratio of 1:2 (Scheme 8).

The use of only one equivalent of borohydride leads to the monoreduced adduct (Scheme 9).

Chlorophosphanes (Scheme 10(a) [11] and Scheme 10(b) [48]) and dimethylphosphinyl chloride (Scheme 10(c) [11]) can be reduced with sodium borohydride.

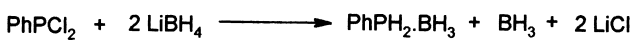
Later, Köster and Morita [49] have shown that triphenylphosphane oxide on treatment with amine–borane at 120 °C is converted into triphenylphosphane–borane.

Imamoto et al. [50–53] have developed a new approach based on a one-pot reduction of phosphane oxides followed by complexation without isolation of the intermediate phosphane (Scheme 11).

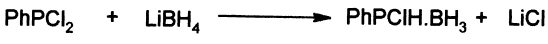
Several tertiary phosphane–boranes can be prepared with good yields by this method. Secondary phosphane oxides and phosphinic esters also reacted under similar conditions to give secondary phosphane–boranes (Scheme 12).

Since the reaction does not proceed in the absence of cerium(III) chloride, it was concluded that trivalent cerium not only activates phosphane oxide reduction, but also facilitates the reaction between the phosphane and $NaBH_4$.

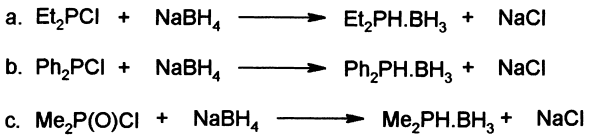
This study also demonstrated the synthesis of secondary symmetrical phosphane–boranes from chlorophosphanes (Scheme 13(a)) or dissymmetrical phosphane–



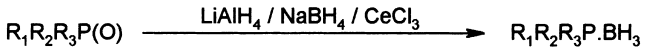
Scheme 8.



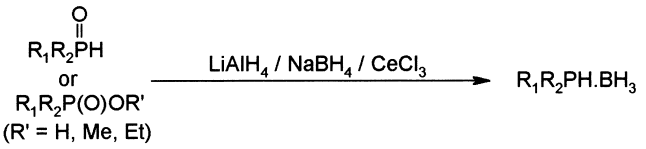
Scheme 9.



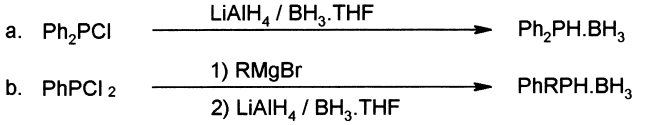
Scheme 10.



Scheme 11.



Scheme 12.



Scheme 13.

boranes from phenyldichlorophosphane by sequential treatment with a Grignard reagent, $LiAlH_4$, and BH_3.THF (Scheme 13(b)).

However, this method could not be successfully applied to the preparation of primary phosphane–borane adducts [42].

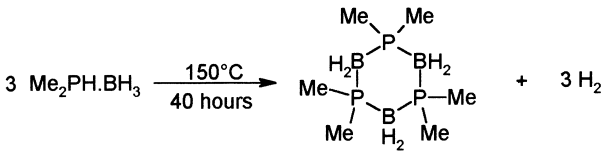
Finally, it should be noticed that $LiAlH_4$ reduction of $Ph_3P.BCl_3$ has been reported to give triphenylphosphane–borane in 50% yield [9].

3. Thermal stability of phosphane–borane complexes

Although phosphane–borane adducts are stable compounds, with the notable exception of $Ph_3.BH_3$ and $PF_3.BH_3$ which dissociate readily at room temperature, their pyrolysis leads to highly stable polymers. Thus, the heating of dimethylphosphane–borane adduct results in the loss of H_2 and the formation of a cyclic trimer as the major product (Scheme 14) [5].

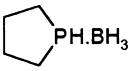
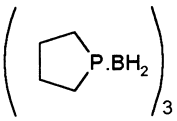
This feature appears to be quite general for secondary phosphane complexes, and the temperature needed for polymerization depends on the structure of the starting material. Table 1 displays the other results reported.

The use of primary phosphane adducts gave only poorly characterized products [47], whereas $P_2H_4.BH_3$ yields $H_3P.BH_3$ and $H_2PH(BH_3)PH_2$ [22,23]. Compounds with amino or silicon groups on phosphorus lead to polymers with cleavage of this heteroatom–phosphorus bond, whereas triphenylphosphite–borane yields one equivalent of phenol and a polymeric phosphorus compound [17].



Scheme 14.

Table 1

Starting adduct	Pyrolysis conditions (°C/h)	Products and yield (%)	Ref.
$Me_2PH.BH_3$	150/40	$(Me_2P.BH_2)_3$(90) + $(Me_2P.BH_2)_4$(9)	[5]
$(CF_3)_2PH.BH_3$	22/96	$[(CF_3)_2P.BH_2]_3$(78)	[8]
$Ph_2PH.BH_3$	170/4	$(Ph_2P.BH_2)_n$(96)	[48]
	200/2	$(Ph_2P.BH_2)_3$(82)	[10]
$(Me_2N)PMe_2.BH_3$	200/30	$(Me_2P.BH_2)_3$(23)	[11]
$Et_2P(SiMe_3).BH_3$	200/2	$(Et_2P.BH_2)_3$(89)	[18]
n-$Bu_2P(SiMe_3).BH_3$	200/2	(n-$Bu_2P.BH_2)_3$(90)	[18]
	198/46		[12]
$Me_2P(BH_3)$–$P(BH_3)Me_2$	290/11	Me_2PH(4) + $(Me_2P.BH_2)_3$(49) + $(Me_2P.BH_2)_4$(35)	[24]
Me_2P–$PMe_2.BH_3$	174/70	Me_2PH(97) + $(Me_2P.BH_2)_{3and4}$(42)[a]	[24]

[a] Yields based on recovered materials.

Condensed ring products are obtained on co-heating a mixture of primary and secondary phosphane adducts [54], or by treating a mixture of Et_2PCl and $EtPCl_2$ with $NaBH_4$, followed by heating [11]. The same procedure was applied to a mixture of Ph_2PCl and $PhPCl_2$ [48].

The stability of tertiary phosphane–boranes is more important, as demonstrated by comparison of the enthalpies of formation of mono-, di- and triphenylphosphane–borane [9]. This value increases with the number of phenyl groups bonded to phosphorus. Accordingly, triphenylphosphane–borane is unaltered even after heating at 150 °C for three hours with concentrated HCl; on the other hand, $Me_3P.BH_3$ decomposes only on heating to 260 °C for 174 h, yielding exclusively H_2, BH_3 and trimethylphosphane [5], showing that the main decomposition involved the BH_3 group.

4. Decomplexation of phosphane–borane complexes

As will be discussed in Section 6, phosphane–borane adducts can be transformed into other complexes, in a variety of ways. The further removal of borane from these complexes will lead to functionalized tricoordinated phosphorus compounds. Thus, the overall process corresponds to the use of borane as a protecting group for phosphanes. Decomplexation must therefore be effected as simply as possible.

The reaction of a phosphane–borane adduct with an amine is an equilibrated reaction (Scheme 1, Section 2.2). Although the distribution of this equilibrium

depends on the relative strength of the amine and the phosphane, the reverse reaction can be used for the decomplexation of the phosphane adducts to obtain the corresponding tricoordinated phosphorus compound. The first examples were reported by Imamoto [50,51] through the use of a large excess of diethylamine or morpholine.

However, the use of a secondary amine is not compatible with all functional groups which may be present in the starting phosphane–borane. This difficulty was first overcome by Le Corre et al. [55] who reported the use of DABCO (diazabicyclo[2.2.2.]octane) or TMEDA (tetramethylethylenediamine) for the decomplexation of carbonyl-containing adducts. Their results show that DABCO in toluene is the most efficient reagent. This combination has also been used for the synthesis of an optically pure diphosphane from its bisborane adduct [56]. The beneficial use of DABCO was also exemplified by a recent study involving phosphane–borane complexes built from fullerenes [57].

However, decomplexation of phosphane–boranes containing α-hydroxy groups gave miscellaneous results [42].

McKenstry and Livinghouse [58,59] reported the use of tetrafluoroboric acid as a complementary method for the removal of borane from phosphane–borane complexes which are unreactive toward aminolysis. This seems particularly suited for borane adducts of electron-rich phosphanes.

5. Characterization of phosphane–borane complexes

5.1. Spectroscopies

5.1.1. IR spectroscopy

The B–H bond stretching frequencies have been measured for a great number of compounds [17,18,26,28,32,38,44,60–63]. The usual pattern is constituted by a strong absorption between 2450 and 2350 cm^{-1}, and a shoulder at 2380–2330 cm^{-1}. The exact frequency depends on the nature of the substituents on phosphorus (alkyl, amino or alkoxy groups), but varies in a narrow range, however. The basicity of a series of phosphites has been correlated with B–H stretching frequencies of their borane adducts [64]. A detailed IR and Raman spectra analysis for dimethylchlorophosphane–borane has also appeared [19].

On the other hand, the P–B bond stretching frequency was reported less often, despite the fact that it is believed to be a much more sensitive criterion of bond strength. Its value usually lies in the range between 518 and 860 cm^{-1} [19,60,62].

5.1.2. NMR spectroscopy

The ^{11}B NMR and ^{31}P–^{11}B coupling data have been collected and discussed by Nöth and Wrackmeyer [65]. Most of these ^{11}B signals appear as a quartet due to the ^{11}P–^{11}B coupling. In some cases, for example $(MeO)_3P.BH_3$, $(Me_2N)_3P.BH_3$ and $(MeO)_2PF.BH_3$ [65], the ^{31}P–^{11}B and ^{11}B–^{1}H coupling constants equalize, so the resulting signal is a simple quintet.

The chemical shifts of phosphane–boranes are centered at -40 ± 5 ppm, and

examination of a series of homologues shows an increase in shielding with the following trends [65]:

$$PMe_3 < HPMe_2 < H_2PMe < PH_3$$

$$PH_3 < HPF_2 < PF_3$$

$$PMe_3 < P(NMe_2)_2 < P(OMe)_3 < PF_3$$

A correlation between the ^{31}P–^{11}P coupling constant of the adduct and the base strength of the starting phosphane has been found [66,67].

^{11}B and ^{1}H NMR spectroscopy have proved useful for the examination of equilibrium distributions between phosphane–borane and amines [68].

^{1}H NMR spectra usually display a quartet (^{1}H–^{11}B coupling) which is further split into a doublet by ^{1}H–^{31}P coupling. In some cases other couplings are also measured, e.g. ^{1}H–^{19}F in $CH_3OPF_2.BH_3$ [66].

Finally, ^{31}P–$\{^{1}H\}$ NMR spectra usually display a quartet due to the ^{11}B–^{31}P coupling. Complexation of borane with a tricoordinated phosphorus compound results in a modification of its ^{31}P chemical shift [62–66]. The difference between the chemical shift of the free tricoordinated phosphorus compound and the chemical shift of its borane adduct is called the coordination chemical shift (*CCS*), which varies depending on the nature of the groups bonded to phosphorus. Several compounds have been compared [66], and it appear that trialkyl- or triarylphosphanes complexation with borane results in a rather strong deshielding ($CCS = 95$ to 133 ppm), whereas aminophosphane and phosphites undergo shielding ($CCS = -3$ to -53 ppm). A tentative interpretation of such variations was also given [66]. Recent NMR data for substituted aryldimethylphosphane–boranes have been correlated with Hammet σ constants [69].

Finally, it should be pointed out that a solid-state NMR study analysis of phosphane–boranes has been recently performed [70].

5.2. Structural analysis

5.2.1. Theoretical features

The unusual stability of phosphane–borane complexes, with respect to amino–borane complexes (for example inertness towards oxygen, moisture, and even sometimes to strong acids and bases; nonhydridic character of the BH_3 hydrogen atoms) [33] has been ascribed to the low polarities and polarizabilities of the P–B and B–H bonds. At first, the P–B bond was described in terms of a "simple" or "classical" σ dative bond, supplemented by a d_π–p_π bonding (back-donation) between occupied p-type orbitals on boron, and unoccupied d-type orbitals on phosphorus [71–74].

However, in the 1970s, the importance of d orbitals in such adducts was minimized, and *ab initio* calculations showed that d contribution is much smaller in a P–B bond than in a P=O bond [62,75]. Moreover, the good agreement between semi-empirical calculations and photoelectron spectroscopy data indicated that rationalization can be effected without any d_π–p_π bonding considerations [76].

In the last years, it has been shown that d orbitals are not involved (or are not necessary) to describe bonding in phosphorus [77] or sulfur [78] compounds. In P=O bonds (which are usually compared to the P–B bond [62,75]) π-type orbital overlap is no more assigned to a "backbonding from the oxygen lone pair into low-lying empty d orbitals". Nowadays, this backbonding is considered to occur into σ* orbitals (LUMO orbitals in a phosphane moiety, e symmetry) [77]. We can reasonably think about a same type of overlap in a P–B bond. Unfortunately, to our knowledge there is no complete theoretical study explaining the differences in reactivity between phosphane–borane and amino–borane adducts.

Few theoretical studies were reported: a detailed MNDO study of methylated and fluorinated phosphane–borane complexes is in good agreement with photoelectron spectroscopy [79]; a recent work using *ab initio* molecular orbital calculation gives informations on the changes in bond dissociation energies upon coordination by Lewis bases (phosphanes, amines, ethers, thioethers), but there is no conclusion on the chemical differences of these adducts [80].

5.2.2. Geometry and X-ray data analysis

An important parameter of the P–B bond is the distance between these atoms. As depicted in Table 2 and Fig. 1, P–B distance ranges from 1.832 to 1.983 Å. In a short overview, alkyl- and arylphosphane–borane complexes give rather long distances, while fluorophosphane–borane complexes exhibit the shortest distances. The P–B bond length appears to decrease with increasing electronegativity of the substituents on phosphorus [62,71,81]. However, the numerous X-ray diffraction analyses performed recently seem to demonstrate that additional factors must be taken into account: (i) the nature of the atoms directly bonded to phosphorus; (ii) the sum of bond angles around phosphorus, since coordination of alkylphosphane with borane results in a decrease of bond length around phosphorus, and an increase of bond angles [71].

In borane adducts of PR_3, (R = H, alkyl, aryl) **6–22** (Scheme 15), the average P–B length is 1.919 Å, with a minimum value of 1.88 Å (compound **18**) and a maximum value of 1.983 Å (compound **14**), the largest ever reported. In adduct **14**, the wide P–B distances (1.960, 1.964 and 1.983 Å) may be due to an electronic effect of the silicon atom located in a β position from the phosphorus atom, and even a steric effect (phenyl and *tert*-butyl substituents at phosphorus). Except in complex **14**, P–B distances are very close to the average value (1.914 ± 0.034 Å). Plotting the sum of bond angles around phosphorus vs P–B bond length in Fig. 2 indicates no direct correlation between these parameters (correlation coefficient = 0.219).

In borane complexes of $R'OPR_2$, (R′,R = alkyl, aryl) **23–26** (Scheme 16), the average P–B length is 1.907 Å, with a minimum value of 1.885 Å (compound **24**) and a maximum value of 1.92 Å (compound **25**). The small P–B bond length in **24** has been accounted for by an intermolecular interaction in the crystal structure between boron (from BH_3) and a hydrogen atom of a second molecule [95]. Except for this particular bond, there is a very weak scattering in this series (average value 1.911 ± 0.013 Å). In contrast with phosphane adducts, a quite good correlation between the sum of bond angles around phosphorus vs P–B bond length is observed

Table 2
X-ray structural data for organophosphorus–borane complexes

Compound	Substituents at phosphorus atom			Length (Å)	ESD[a]	Sum of angles[b]	Ref.
7	H	H	H	1.930	0.010	–	[82,83]
	H	H	H	1.937	0.005	303.6	[84][c]
8	alkyl	alkyl	alkyl	1.905	–	–	[85]
	alkyl	alkyl	alkyl	1.904	–	–	[85]
9	alkyl	alkyl	alkyl	1.917	0.007	312.3	[86]
10	alkyl	alkyl	alkyl	1.901	0.007	315.0	[71][c]
11	alkyl	alkyl	alkyl	1.927	0.007	315.4	[87]
10	alkyl	alkyl	H	1.919	0.003	–	[43]
13	alkyl	H	H	1.906	0.006	306.3	[71][c]
14	aryl	alkyl	alkyl	1.960	–	318.5	[88]
	aryl	alkyl	alkyl	1.964	–	318.5	[88]
	aryl	alkyl	alkyl	1.983	–	316.0	[88]
15	aryl	alkyl	H	1.944	0.008	311.3	[89]
16	aryl	aryl	alkyl	1.926	–	315.0	[34]
17	aryl	aryl	alkyl	1.936	0.003	311.9	[90]
18	aryl	aryl	alkyl	1.880	–	–	[91]
	aryl	aryl	alkyl	1.900	–	–	[91]
19	aryl	aryl	alkyl	1.887	0.009	–	[92]
	aryl	aryl	alkyl	1.933	0.007	–	[92]
	aryl	aryl	alkyl	1.926	0.007	–	[92]
20	aryl	aryl	alkyl	1.917	0.002	313.5	[93]
	aryl	aryl	alkyl	1.916	0.002	315.1	[93]
21	aryl	aryl	alkyl	1.900	0.010	311.7	[93]
	aryl	aryl	alkyl	1.900	0.010	313.9	[93]
	aryl	aryl	alkyl	1.890	0.010	311.9	[93]
	aryl	aryl	alkyl	1.890	0.010	315.6	[93]
22	aryl	aryl	aryl	1.930	0.010	320.3	[94][d]
	aryl	aryl	aryl	1.900	0.020	317.5	[94][d]
6	aryl	aryl	aryl	1.930	0.010	315.2	[46]
23	aryl	aryl	O	1.915	–	313.8	[56]
24	aryl	aryl	O	1.914	0.005	310.4	[95]
	aryl	aryl	O	1.908	0.005	310.7	[95]
	aryl	aryl	O	1.885	0.006	312.5	[95]
25	aryl	aryl	O	1.920	0.010	312.2	[96]
26	aryl	alkyl	O	1.898	0.004	303.7	[96]
27	alkyl	alkyl	N	1.922	0.009	–	[97]
28	aryl	alkyl	N	1.900	0.010	319.2	[61]
29	aryl	aryl	N	1.916	0.003	322.7	[98]
	aryl	aryl	N	1.902	0.004	314.1	[98]
30	aryl	aryl	N	1.930	0.010	325.4	[61]
31	aryl	aryl	N	1.879	0.010	309.1	[99]
32	aryl	aryl	N	1.925	0.006	308.6	[99]
33	aryl	aryl	Fe	1.949	0.007	323.8	[100]
34	alkyl	alkyl	P	1.968	0.016	313.3	[101][d]
	alkyl	alkyl	P	1.927	0.016	315.9	[101][d]
	alkyl	alkyl	P	1.957	0.017	315.0	[101][d]
35	aryl	O	O	1.895	0.008	307.3	[102]
36	aryl	O	O	1.912	0.004	312.1	[103][d]
	aryl	O	O	1.897	0.005	309.9	[103][d]

Table 2 (*continued*)

Compound	Substituents at phosphorus atom			Length (Å)	ESD[a]	Sum of angles[b]	Ref.
37	aryl	O	N	1.869	0.007	309.5	[103]
38	aryl	O	N	1.917	0.004	311.4	[104]
39	aryl	N	N	1.910	0.003	307.0	[105]
40	O	O	O	1.884	0.011	322.1	[106]
41	O	O	O	1.879	0.017	313.0	[81]
42	O	O	N	1.873	0.007	306.6	[107,108]
43	N	N	N	1.858	0.005	306.6	[109]
44	N	N	N	1.980	0.030	306.0	[110]
45	N	N	N	1.887	0.013	316.5	[111]
46	F	F	H	1.832	0.009	–	[112][c]
47	F	F	F	1.836	0.012	–	[113][c]

[a] Estimated standard deviation, when available.
[b] Sum of bond angles around phosphorus atom.
[c] Structural data were determined by microwave spectroscopy.
[d] Two molecules per crystal.

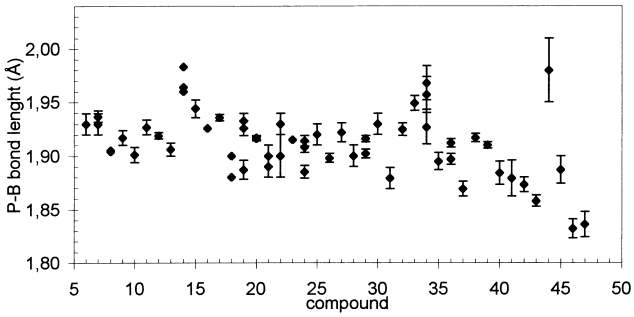
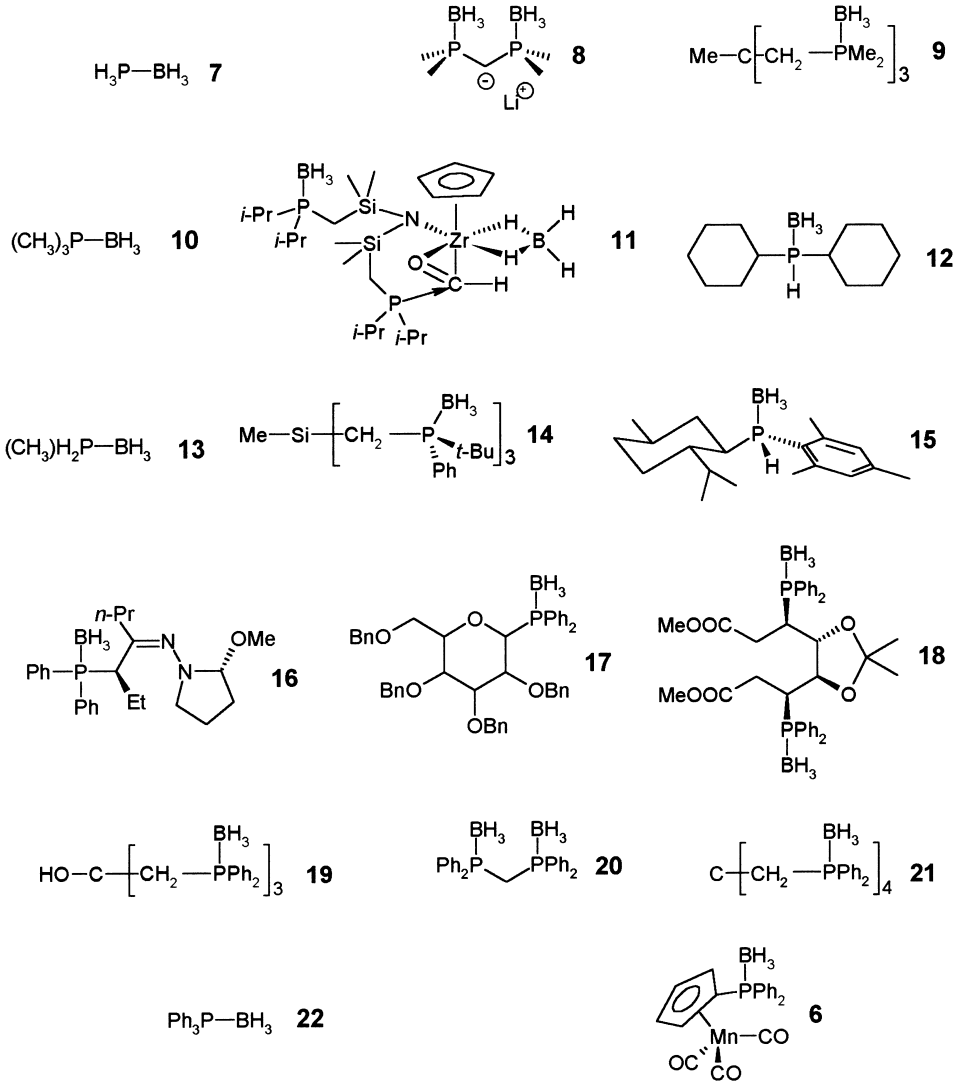


Fig. 1. Dispersion of P–B bond length.

[Fig. 3, correlation coefficient = 0.892, the value 1.885 Å (adduct **24**) has been discarded].

Borane adducts of (R′R″N)PR_2, (R′,R″,R = alkyl, aryl) **27–32** (Scheme 17), exhibit an average P–B length of 1.911 Å, with a minimum value of 1.879 Å (compound **31**) and a maximum value of 1.93 Å (compound **30**). Although complexes **31** and **32** possess the same substituents around phosphorus, and the same cyclic structure (same sum of bond angles around phosphorus), P–B bond lengths are very different (1.879 and 1.925 Å, respectively). The higher value for compound **32** may be due to an electronic effect of a silicon atom bonded to the nitrogen atom in a β position from the phosphorus atom. With the exception of this adduct, there is a very good correlation between the sum of bond angles around phosphorus vs P–B bond length (Fig. 4, correlation coefficient = 0.945).

In the last series of adducts **33–47** (Scheme 18), the lack of data for each kind of organophosphorus borane adduct (phosphite, triaminophosphane,...) do not allow a qualitative interpretation of the observed variations in P–B bond length and angles.



Scheme 15.

Rather long P–B bond distances are observed in adducts formed with P- and Fe-bonded phosphanes (compounds **33, 34**). In this series, the previously assumed trend, i.e. the decrease of P–B bond length when increasing the number of electronegative heteroatoms around phosphorus, seems to be respected. Thus, the shortest bond distances (1.832 and 1.836 Å) are reported for trifluoro- and difluorophosphane–borane complexes **46** and **47**. However the rather similar complexes **43** and **44** exhibit very different P–B bond distances (1.858 Å vs 1.98 Å). In these series, no

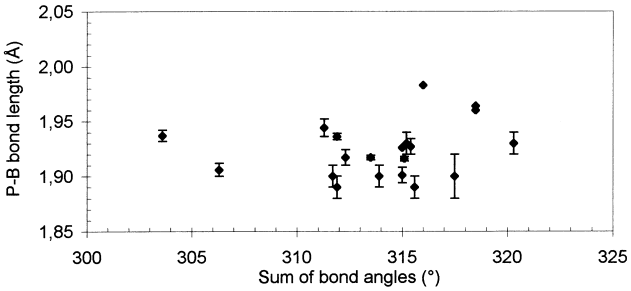
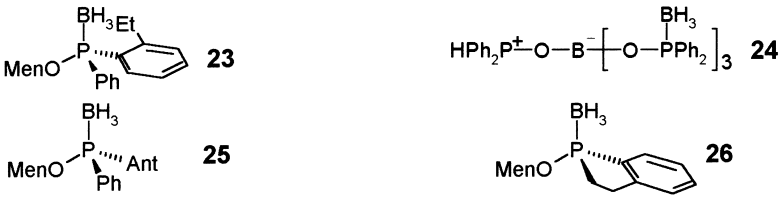


Fig. 2. Plot of P–B bond length vs sum of bond angles around phosphorus in $H_3B.Pr_3$ (R = H, alkyl, aryl).



Scheme 16.

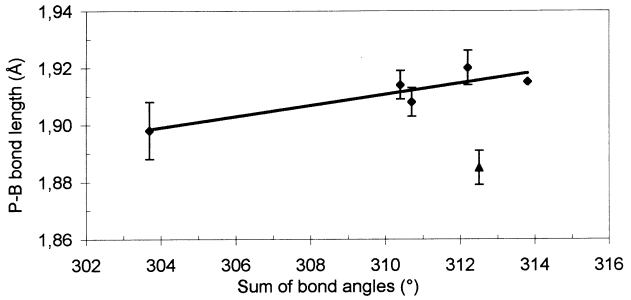
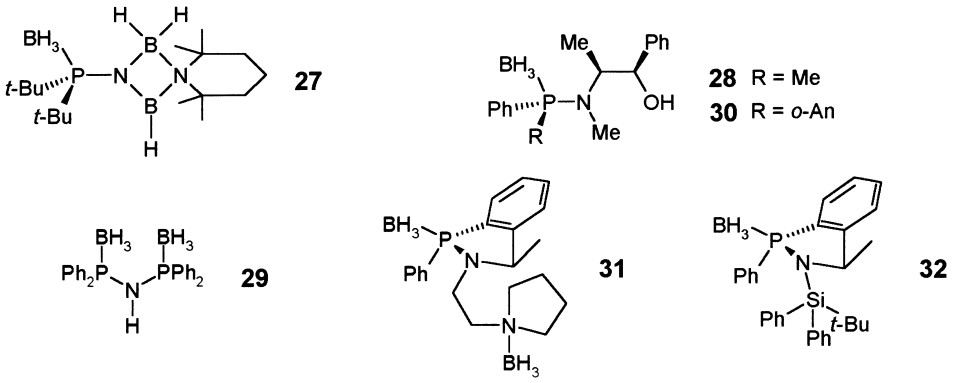


Fig. 3. Plot of P–B bond length vs sum of bond angles around phosphorus in $H_3B.P(OR')R_2$ (R′,R = alkyl, aryl).

apparent correlation between the sum of bond angles around phosphorus vs P–B bond length may be proposed (Fig. 5).

6. Synthetic applications

Constituting a unique class of organophosphorus compounds, phosphane–boranes have attracted the attention of chemists and revealed their peculiar chemical properties. In this part, we will describe the reactivity of these compounds demonstrating that they have potential utility as reagents and also as useful intermediates in synthetic organic chemistry.



Scheme 17.

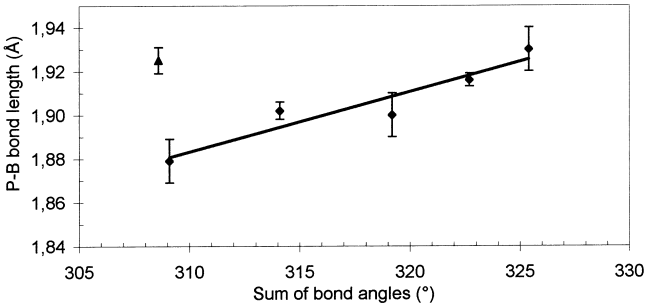


Fig. 4. Plot of P–B bond length vs sum of bond angles around phosphorus in $H_3B.P(NR'R'')R_2$ (R′,R″,R = alkyl, aryl).

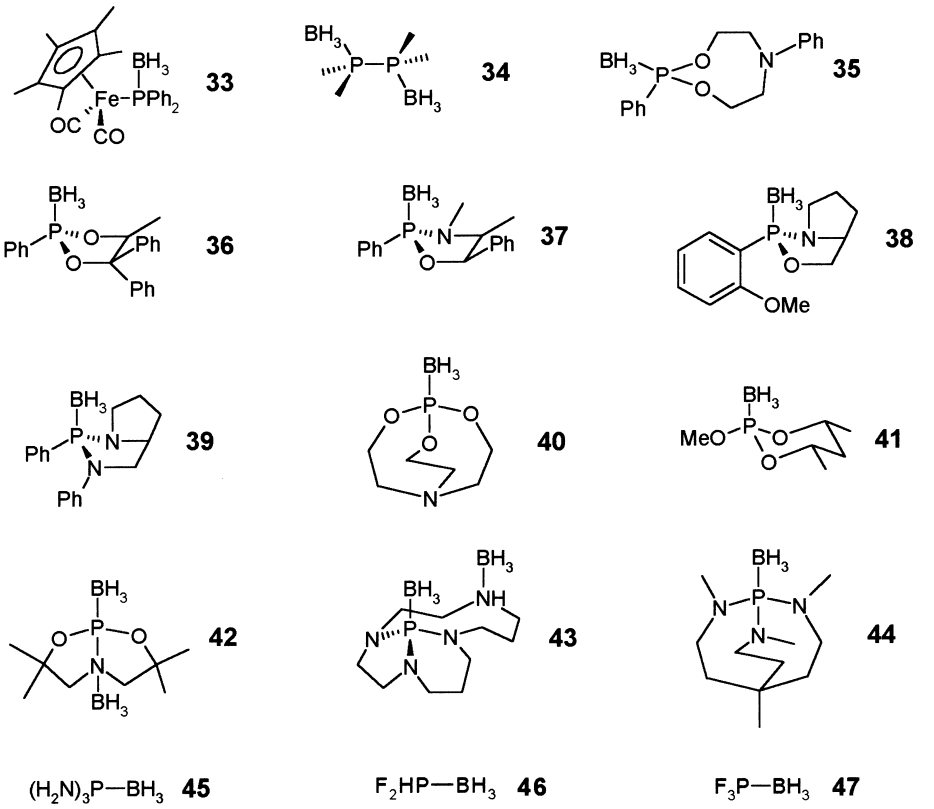
6.1. Borane as efficient phosphorus protecting group

Phosphanes are very sensitive to oxidizing agents, thus the synthesis of functionalized phosphanes cannot include an oxidation step. Phosphane–borane complexes have appeared to be insensitive to the usual oxidizing reagents and have permitted the oxidation of β-hydroxyalkyldiphenylphosphane–boranes in good chemical yield [114] (Scheme 19).

Moreover, the oxidation may be controlled to obtain carbonyl- or carboxy phosphane–boranes (Scheme 20).

The efficient role of borane as protecting group is also well illustrated in the scalemic synthesis developed by Imamoto et al. of industrially important bis(phosphanes) such as DIPAMP [52] (Scheme 21).

Based on these results, Imamoto has realized the synthesis of a variety of functionalized phosphane–boranes by using methyldiphenylphosphane–borane as a model substrate. The compound was metalated with *sec*-BuLi in THF at 78 °C, and the generated carbanion reacted with various electrophiles to give functionalized phosphane–boranes [33,52,56,115–118] (Scheme 22).



Scheme 18.

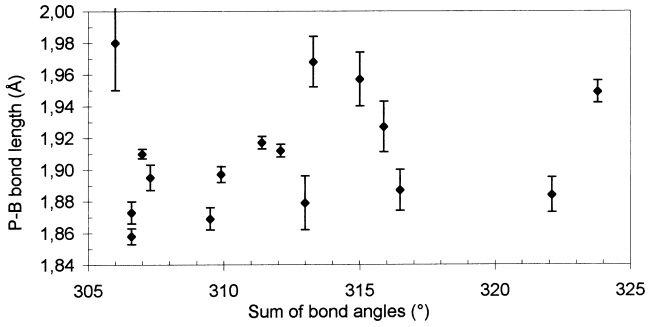
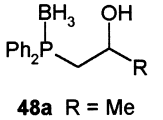
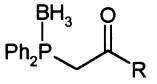


Fig. 5. Plot of P–B bond length vs sum of bond angles around phosphorus in adducts **28–42**.

Recently, Evans et al. have reported the enantioselective deprotonation of aryldimethylphosphane–borane complexes for the synthesis of C_2-symmetric P-chiral diphosphanes with enantioselectives up to 99% ee, using *sec*-BuLi-(−)sparteine



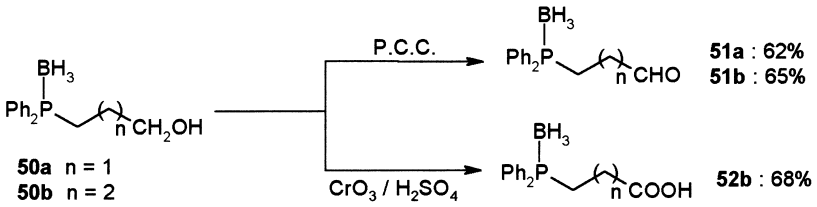
CrO_3 / H_2SO_4
or
P.C.C. (Corey's reagent)



48a R = Me
48b R = Ph

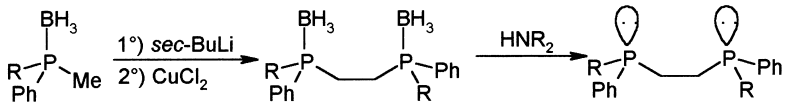
Product	Jone's reagent	Corey's reagent
49a	56%	72%
49b	52%	78%

Scheme 19.



50a n = 1
50b n = 2

Scheme 20.

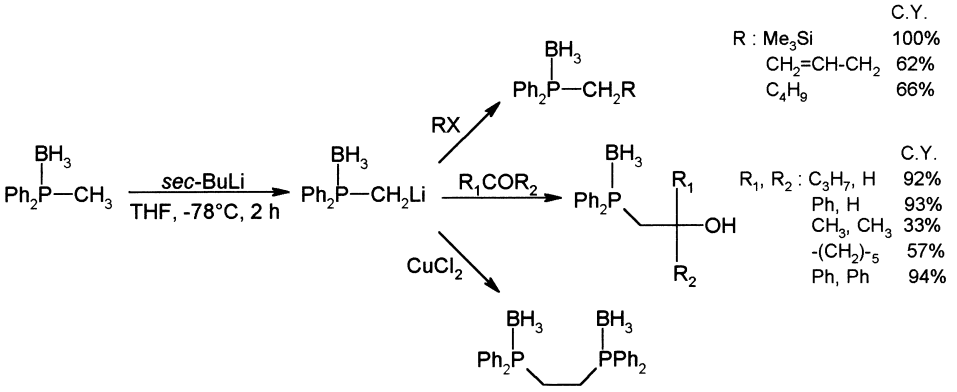


(*R*)-**53a** R = *t*-Bu
(*S*)-**53b** R = *o*-An

(*R, R*)-**54a** R = *t*-Bu
(*S, S*)-**54b** R = *o*-An

(*R, R*)-**55a** R = *t*-Bu
(*S, S*)-**55b** R = *o*-An

Scheme 21.

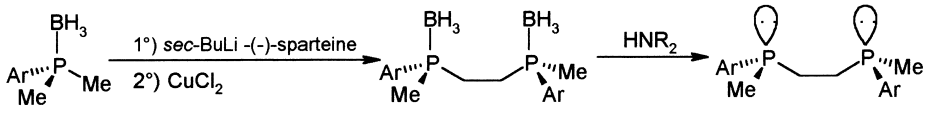


Scheme 22.

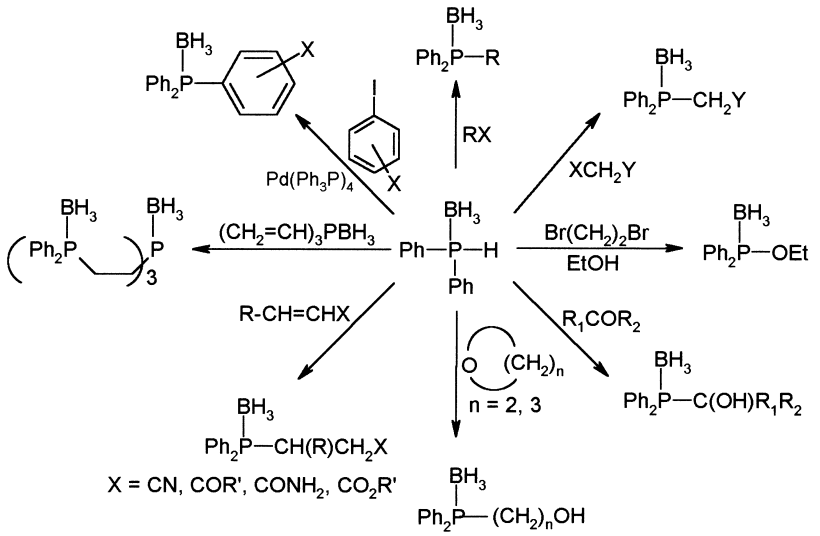
complex as chiral base for the asymmetric metallation of the phosphane–borane substrate [119] (Scheme 23).

Moreover, the reaction of diphenylphosphane–borane with various nucleophiles proceeded under mild conditions providing a new variety of organophosphorus–borane complexes (Scheme 24).

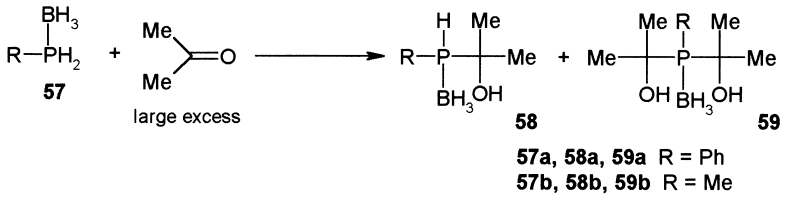
A similar procedure has been recently described by Gaumont et al. on primary phosphane–boranes which constitute interesting new tools in the field of organic chemistry [42,120]. They can be considered as synthetic equivalents of [R–P$^-$–H] *via* selective mono-alkylation/deprotection reactions of [R–P$^-$–] *via* α,α′-dihydrophosphination/deprotection reactions. Nevertheless, contrarily to the results described by Imamoto, the use of *n*-BuLi is not necessary to activate the phosphane–borane complex. Thus, the P–H activation induced by the BH_3 group is observed in the preparation of propanone adducts. If hydrophosphination is the major process observed in all the reactions with aldehydes and propanone, a competitive hydroboration reaction has been also reported as a minor process (Scheme 25 and Table 3).



Scheme 23.



Scheme 24.



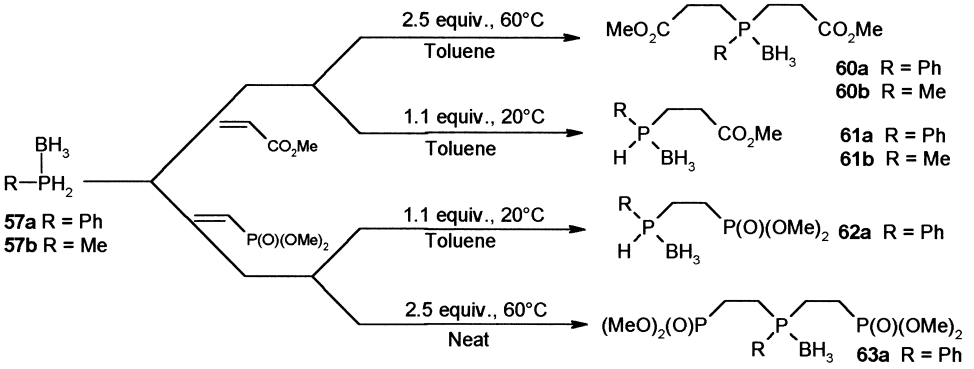
Scheme 25.

Table 3
Reactivity of phosphane–boranes **57a** and **57b** towards aldehydes and propanone

Entry	Phosphane–boranes	Carbonyl compound	1.1 equiv. of carbonyl compound	3 equiv. of carbonyl compound
1	**57a**	PhCHO	**58c**: 55%; **59c**: 15%	**58c**: 20%; **59c**: 70%
2	**57a**	EtCHO	**58d**: 4%; **59d**: 48%	**58d**: 5%; **59d**: 75%
3	**57b**	PhCHO	**58e**: 8%; **59e**: 46%	**58e**: 6%; **59e**: 92%
4	**57a**	$(CH_3)_2C{=}O$	**58a**: 14%; **59a**: 0%	**58a**: 55%; **59a**: 5%
5	**57b**	$(CH_3)_2C{=}O$	**58b**: 8%; **59b**: 12%	**58b**: 41%; **69b**: 44%

The uncatalyzed hydrophosphination of vinylic esters allows a selective access to mono-adducts and to symmetrical or unsymmetrical bis-adducts. This methodology should be useful for the preparation of free phosphanes bearing various functional groups, especially for new 1,4-di- or triphosphanes which are important ligands in organometallic chemistry [121] (Scheme 26).

As already mentioned (Section 4), the BH_3 group of phosphane–borane compounds may be removed by treatment with a large excess of an amine and this reaction has been proved to proceed in a stereospecific manner with retention of configuration at the phosphorus atom when a chiral phosphane–borane complex was studied. Thus, the chiral phosphane described by Horner [122] may be protected by a BH_3 group and subsequently deprotected under mild conditions to afford the



Scheme 26.

same product without any racemization at the phosphorus atom [52,115,116] (Scheme 27).

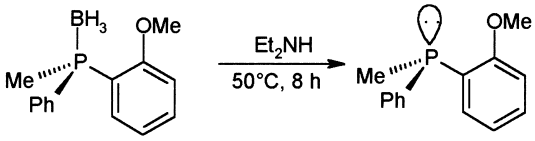
The reactions mentioned above may offer a possible route to such phosphane derivatives that are not easily accessible. It is noteworthy that in these reaction sequences, the borane group acts both as an activating and protecting group (Scheme 28).

Thus, it activates the adjacent hydrogen or methyl group to deprotonation with a strong base and at the same time, it protects the phosphanes which are generally sensitive towards oxygen and electrophiles such as alkyl halides. This approach is applicable to the synthesis of optically active phosphane–borane compounds possessing a P–H bond and easily prepared from dichlorophosphane and a chiral moiety such as (−)-menthol [51,123,124] (Scheme 29).

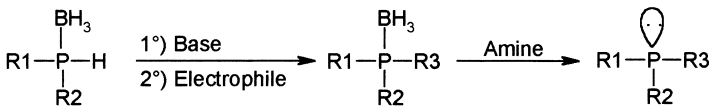
The reactions with alkyl iodides in the presence of NaH proceeded with complete retention of configuration. Furthermore, in the case of aryl iodides, the stereospecificity of the reaction depended largely on the nature of the solvent and of the base used. A complete retention of configuration is observed in acetonitrile and THF against a large inversion when the reaction is performed in diethylether or toluene [52] (Scheme 30).

This approach has been also applied to the multisteps synthesis of various C_2-symmetric bidentate ligands possessing a homochiral phosphane center following a typical procedure described in Scheme 31.

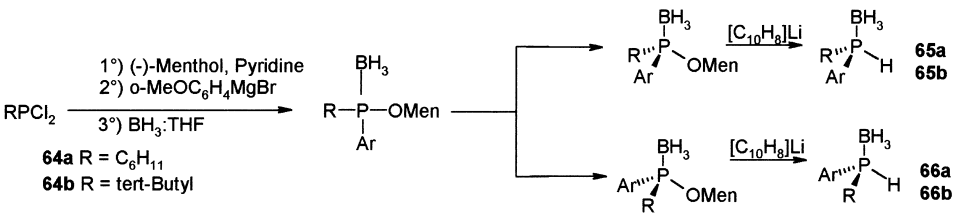
Analogous reactions of methylphosphane–borane with dichlorosilanes were



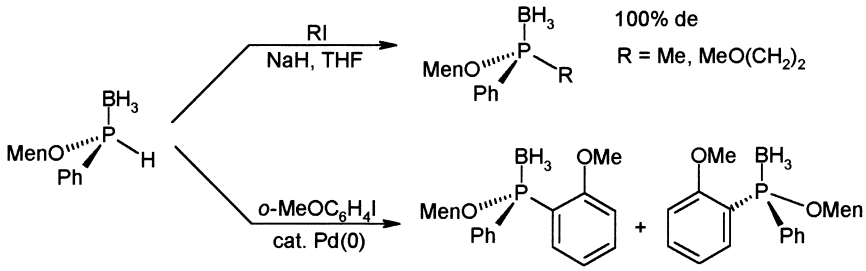
Scheme 27.



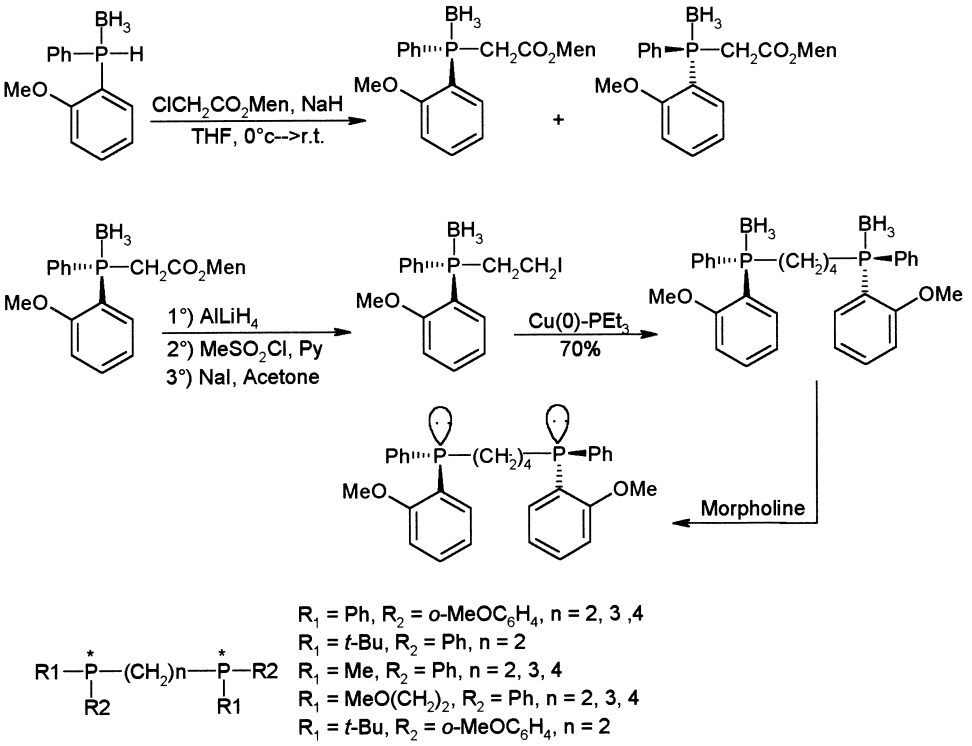
Scheme 28.



Scheme 29.



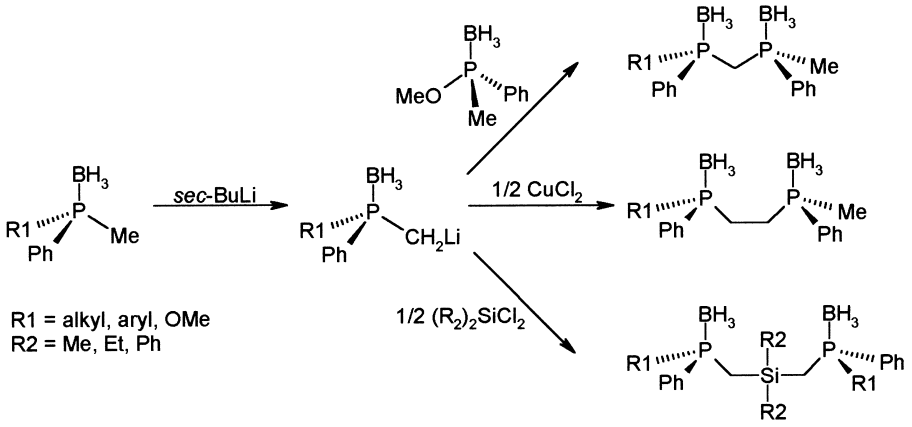
Scheme 30.



Scheme 31.

reported by Jugé et al. to yield cleanly the corresponding 1,1- and 1,3-bis(phosphane) systems [125,126] (Scheme 32).

Despite all these studies, the synthesis of a broad spectrum of chiral organophosphorus borane complexes with P–N, P–O or P–C bonds *via* a highly stereospecific reaction has been described. Thus, an example of this strategy is based on a diastereoselective preparation of an oxazaphospholidine–borane complex derived from (+)-ephedrine (or its enantiomer form (−)-ephedrine) followed by the regio-



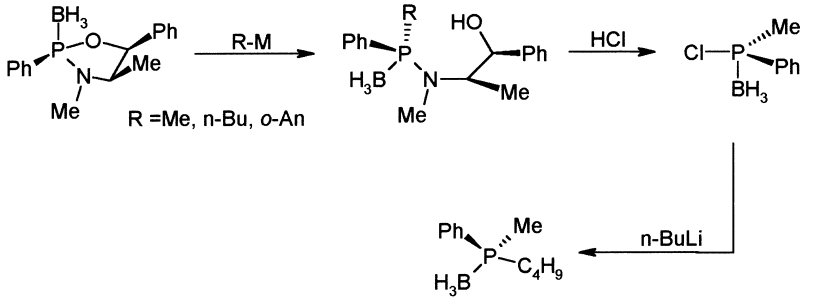
Scheme 32.

and stereoselective P–O bond rupture with various organolithium reagents [61,126] (Scheme 33).

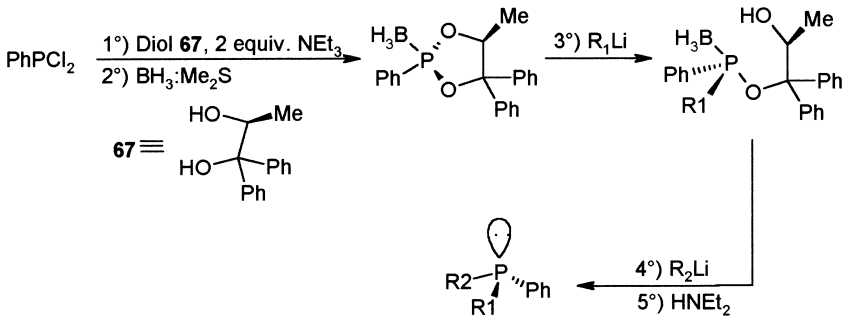
Recently, this reaction has been extended to dioxaphospholane–borane complexes and led to the preparation of chiral tertiary phosphanes in only three steps [127] (Scheme 34).

Another synthetic method of optically active secondary phosphane–borane complexes consists in the reductive removal of the menthyloxy group of diastereomerically pure menthyloxyphosphane–borane complexes at $-78\ ^{\circ}C$ by the use of one electron reductant such as lithium naphthalenide, lithium 4,4′-di-*tert*-butyldiphenylide and Li–NH_3. Thus, the expected products were obtained in almost quantitative yields with an excellent stereoselectivity varying from 81 to 89% ee [128,129] (Scheme 35).

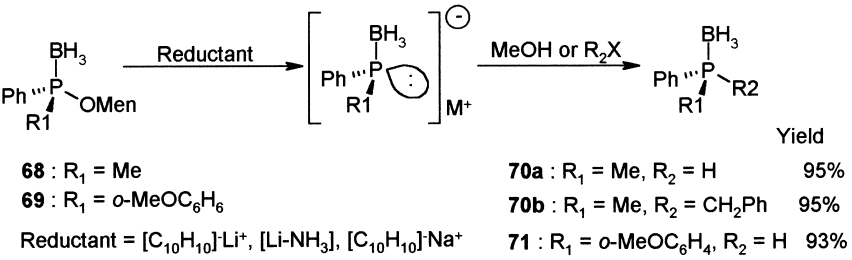
It is noteworthy that the borane group has been extensively used as a protecting group for the synthesis of various different chiral phosphanes [35,55,58,130–138]. Herein, we will report in Scheme 36 the most significant applications described.



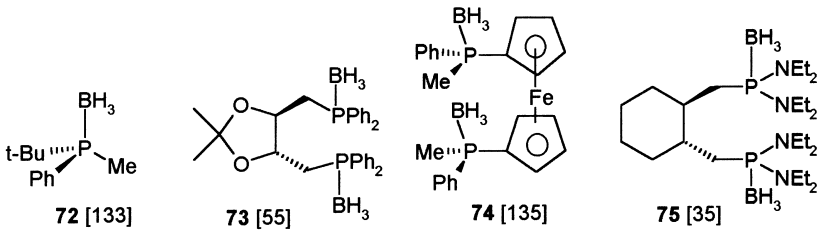
Scheme 33.



Scheme 34.



Scheme 35.

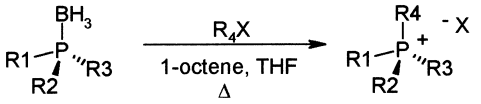


Scheme 36.

6.2. *Phosphane–boranes as reagents in organic synthesis*

6.2.1. *Synthesis of chiral and achiral phosphonium salts*

Although the synthesis of quaternary phosphonium salts is well known [139], it is of particular interest to access to optically active compounds which are usually prepared by resolution of the racemic form [140]. Thus, Jugé et al. have reported the preparation of chiral and achiral phosphonium salts by heating the corresponding phosphane–borane complexes with an alkyl (or aryl) halide in a mixture of 1-octene/THF [141] (Scheme 37 and Table 4).



R_1, R_2, R_3, R_4 : alkyl-aryl

Scheme 37.

Table 4

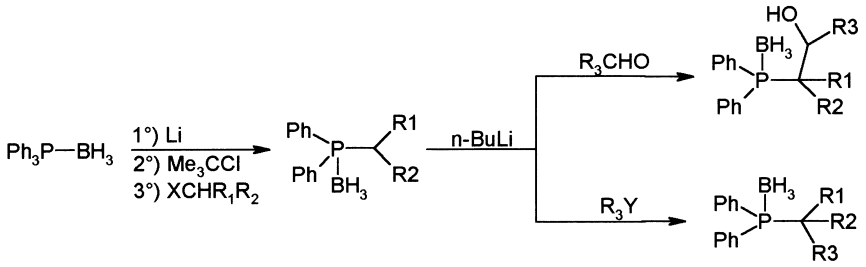
Entry	Phosphane–boranes	Halides	Phosphonium salts	Yield (%)
1	Ph_3P–BH_3	CH_3I	Ph_3P^+—Me, I^-	85
2	$Ph_2PCH_2CH_2PPh_2$ (each P bears BH_3)	CH_3I	$[Ph_2PCH_2CH_2PPh_2]^{2+}$ (each P bears Me), $2I^-$	87
3	o-An, Ph, Me, BH_3 on P	$PhCH_2Br$	o-An, Ph, Me, Benzyl on P^+, Br^-	75
4	o-An, Ph, Me, BH_3 on P	$BrCH_2CN$	o-An, Ph, Me, CH_2CN on P^+, Br^-	50
5	Ph, Ph, BH_3 on P, Br	–	Ph, Ph, Br^- on P^+	90

6.2.2. *Alkylation and olefination reactions*

Phosphane–borane complexes have a reactivity similar to phosphane oxide compounds. Recently, Le Corre et al. have demonstrated this reactivity in an alkylation reaction with various electrophiles leading to new phosphanes [142] (Scheme 38 and Table 5).

Moreover, the activation of these phosphane–borane complexes has been illustrated by an olefination reaction of carbonyl compounds, similar to the Horner reaction with phosphane oxides. Thus, various alkenes have been obtained resulting from condensation of the carbanions, derived from the phosphane–borane complexes and aldehydes (Scheme 39 and Table 6).

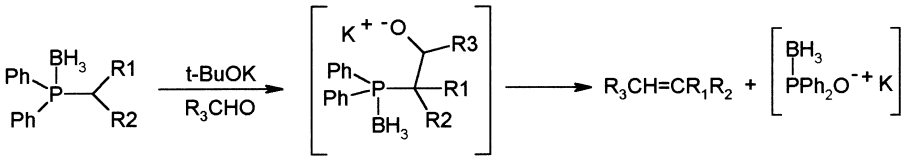
The presence of the BH_3 unit allows a clean deprotonation of 3,4-dimethyl-1-phenylphosphole–borane furnishing a delocalized anion which, upon reaction with



Scheme 38.

Table 5

Entry	R_3Y or R_3CHO	R_1	R_2	R_3	Yield (%)
1	PhCOCl	H	Ph	PhC(O)	86
2	MeI	H	Ph	Me	74
3	$PhCH_2Br$	H	Ph	$PhCH_2$	57
4	MeI	Ph	CH_2Ph	Me	76
5	$(EtO_2O)_2$	H	Ph	$EtO_2CC(O)$	72
6	PhCHO	Ph	H	PhCH(OH)	62



Scheme 39.

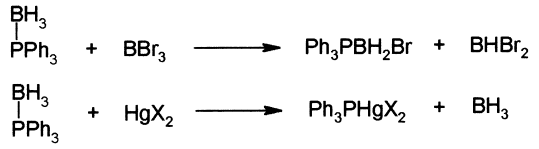
Table 6

Entry	R_1	R_2	R_3	Yield (%)
1	H	CO_2Me	Ph	42
2	H	Ph	Ph	20
3	H	CN	Ph	70
4	Me	Ph	Ph	77
5	H	CO_2Me	C_6H_5–CH=CH	59
6	H	Ph	C_6H_5–CH=CH	63

different electrophiles yields a mixture of α- and γ-alkylated products [41]. The α/γ ratio depends on the nature of the nucleophile.

6.2.3. Functionalization of the borane group in phosphane–boranes

In 1965, Frisch et al. were the first to report the treatment of triphenylphosphane–borane complex by BBr_3 or HgX_2 leading to two new organophosphorus complexes [9] (Scheme 40).

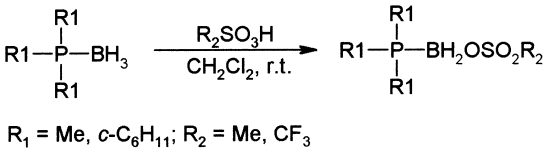


Scheme 40.

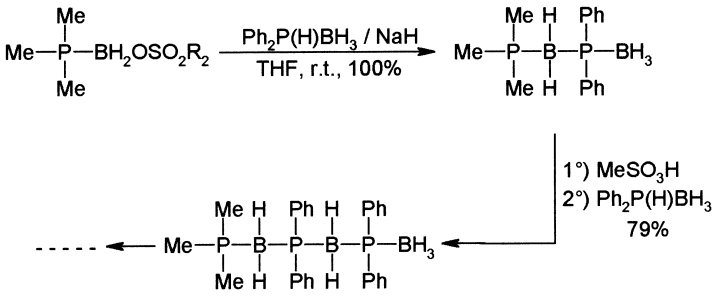
By the same order, Imamoto et al. have reported that phosphane–borane complexes can react with methanesulfonic acid or trifluoromethanesulfonic acid in CH_2Cl_2 to give the corresponding sulfonates [52,115,116,143] (Scheme 41).

Using the substitution reaction on the boron atom, Imamoto has realized the synthesis of a new class of phosphane–borane compounds bearing a P–B bond linkage (Scheme 42).

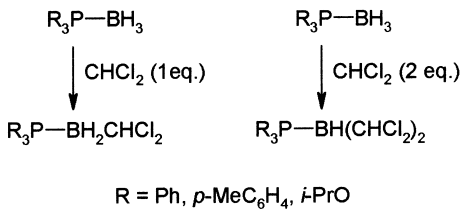
Recently, Foucaud et al. have described the reaction of dichlorocarbene with a phosphane–borane complex leading to the insertion of dichlorocarbene into the B–H bond and formation of new functionalized boranes [144] (Scheme 43).



Scheme 41.



Scheme 42.



Scheme 43.

Under the same conditions Keglevich et al. have realized the synthesis of various phosphane–borane complexes of P-heterocycles in 30–50% chemical yield [37–39] (Scheme 44).

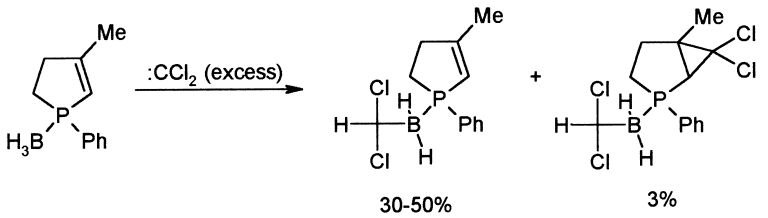
6.2.4. Hydroboration of olefins

In 1981, Pelter et al. reported the use of crystalline triphenylphosphite–borane complex as hydroboration reagent of olefins in mild conditions. This compound completely hydroborated oct-1-ene after 2 h in refluxing dimethoxyethane [30] (Scheme 45).

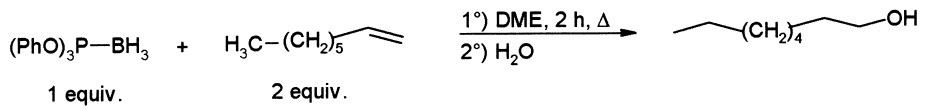
6.2.5. Enantioselective borane reduction of ketones

In 1992, Buono et al. reported the enantioselective borane reduction of ketones using new chiral oxazaphospholidine–borane complexes synthesized from chiral aminoalcohols. The use of a catalytic amount (2 mol%) of complex **76** in the reduction of various ketones by borane led to the corresponding alcohols with enantioselectivities ranging from 33 to 92% ee and quantitative conversion at 110 °C, whereas the reduction proceeded with 99% ee under stoichiometric conditions [145,146] (Scheme 46 and Table 7).

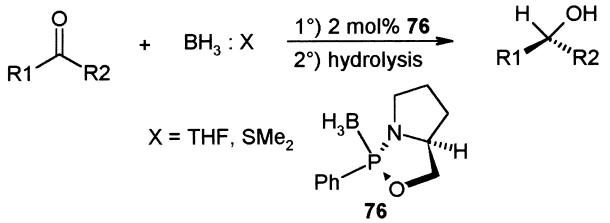
A mechanism has been proposed through a pentacoordinate trigonal bipyramidal phosphorus intermediate suggesting a hydride transfer from the P–BH_3 unit [147].



Scheme 44.



Scheme 45.



Scheme 46.

Table 7
Reduction of ketones with 2 mol% of **76** at 110 °C

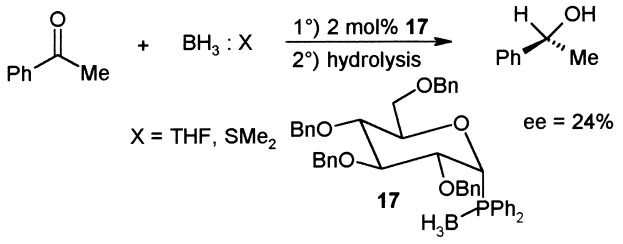
Entry	Ketone	ee (%)	Abs. Conf.	Yield (%)
1	Acetophenone	33	*R*	80
2	Acetophenone[a]	>95	*R*	77
3	Propiophenone	38	*R*	63
4	Benzyl methyl ketone	92	*S*	75
5	*iso*-Propyl methyl ketone	92	*S*	75
6	Ethyl acetoacetate	76	*R*	76
7	2-Acetyl furane	40	*R*	70

[a] Reaction performed using 1 equivalent of oxazaphospholidine–borane complex **76**.

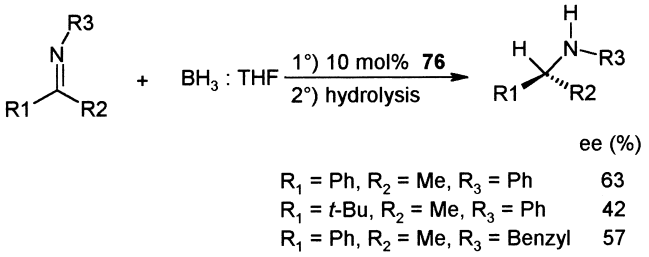
Based on these studies, Vasella et al. have reported the synthesis of a glycosylphosphane–borane complex **17** and its use as catalyst (2 mol%) in asymmetric borane reduction of acetophenone at 110 °C with an enantioselectivity up to 25% ee [90] (Scheme 47).

6.2.6. *Enantioselective borane reduction of imines*

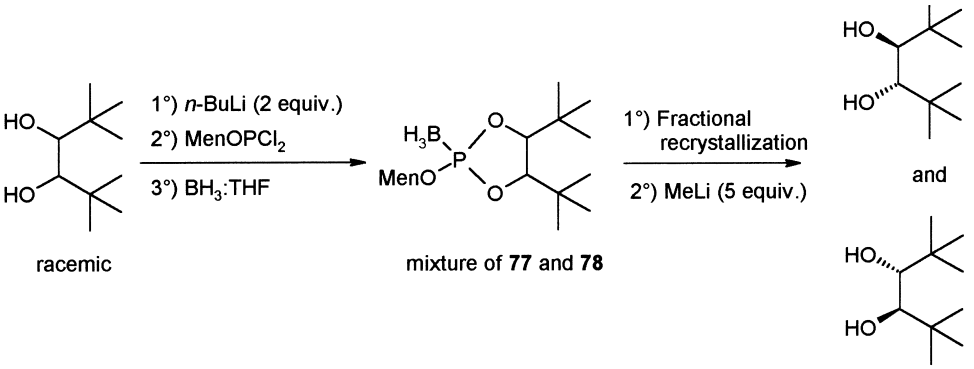
In 1996, the enantioselective borane reduction of imines catalyzed by an oxazaphospholidine–borane complex **76** in refluxing toluene was reported. Thus, optically active amines have been obtained with optical yields up to 63% [148] (Scheme 48).



Scheme 47.



Scheme 48.



Scheme 49.

6.2.7. Resolution of a racemic diol via phosphane–borane

Imamoto [149] has devised a new method for the optical resolution of 2,2,5,5-tetramethyl-3,4-hexanediol, using dichloro(*l*-menthyloxy)phosphine as derivatizing reagent. Separation of the two diastereomers **77** and **78**, and subsequent treatment with methyl lithium afforded the two enantiomerically pure diols (Scheme 49).

7. Conclusion

Phosphine–borane complexes have emerged as a new class of organophosphorus compounds whose reactivity and unusual stability have focused a rapidly growing interest. Numerous studies have investigated the nature of the P–B bond, and the peculiar chemical properties of these adducts. Such features must result from the low polarities and polarizabilities of the P–B and P–H bonds. The literature on phosphane–boranes is rather limited, but in view of their attractive properties, we can expect increasing activity on this subject.

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