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# Boron- and phosporus-containing heterocycles: first evidence of a transient cyclic phosphaborolane with P–H and B–H bonds

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**Abstract**

A stable cyclic phosphine–borane was prepared by an intramolecular regioselective hydroboration of the allylphosphine–borane precursor. Under flash vacuum thermolysis (FVT) conditions, the corresponding transient phosphaborolane was formed and was characterized by high-resolution mass spectrometry using a tandem FVT/MS device.

*Keywords:* Phosphorus; Boron; Phosphaborolane; Flash vacuum thermolysis; Phosphine boranes; Borylphosphines

## 1. Introduction

The reactions of phosphines with boranes have long been studied. Most of the well known structures are four-coordinate both at boron and at phosphorus. Whereas the $R_3P–BH_3$ adducts with tertiary or secondary phosphines are usually stable, the primary phosphine–borane derivatives tend to polymerize. Stabilized three-coordinate borylphosphines have been known for more than 30 years, and new structures have recently been reported [1]. Recent theoretical calculations [2] and experimental measurements [3] demonstrate that the B–P $\pi$-bonding of borylphosphines is at least as strong as the B–N $\pi$-bonding of borylamines (40.5 kcal $mol^{-1}$ for $H_2B–PH_2$ vs. 37.9 kcal $mol^{-1}$ for $H_2B–NH_2$), although inversion barrier at phosphorus is higher than that at nitrogen.

It might be expected from these data that the simplest borylphosphines with BH and PH bonds should be stable in the gas phase. Such structures, unknown so far, are of theoretical interest as phosphorus equivalents of simple boramines and of synthetic interest as potential single-source precursors of boron phosphide [4]. We planned to form them by thermolysis under vacuum of the suitable phosphine–borane precursors. The simple primary phosphine–$BH_3$ adducts are too unstable to be used as starting materials. They usually decompose before subliming, melting or boiling leading to a complex mixture, and with evolution of dihydrogen [5]. Since a t-butyl substituent may be considered to be a masked hydrogen atom (formation of a P–H bond by thermal $\beta$-elimination of isobutene) [6] and a shield which protects the phosphorus from attack by oxygen and water, there was interest in preparing volatile precursors containing one or more t-butyl groups. Thus, $^tBu_2PH \cdot BH_3$, $^tBuPH_2 \cdot BH_3$ and more generally $^t$Bu-PH(R) $\cdot BH_3$ adducts should be considered as synthetic equivalents of the simple $H_2P–BH_2$ and $HP(R)BH_2$ derivatives, respectively. We report here the synthesis, characterization and decomposition studies of various t-butylphosphine–borane adducts.

## 2. Results and discussion

The phosphine precursors **2a,b** were synthesized by reduction of the corresponding *P*-chlorophosphines **1a,b** with $LiAlH_4$ [7]. t-Butylallylphosphine (**2c**) was prepared in a two-step sequence involving reaction of a Grignard reagent with **1a** followed by chemoselective reduction [8] of the P–Cl derivative **1c** thus obtained with dichloroalane ($AlHCl_2$) [9]. Isolated yields were ca. 65–85%. Borane adducts **3a–c** were then obtained in essentially quantitative yields by classical condensa-

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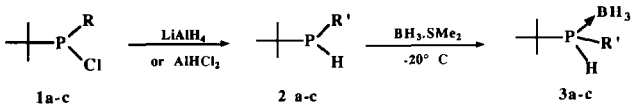
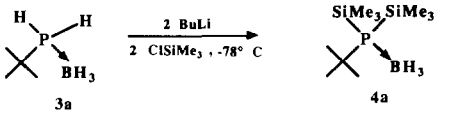



1a : R = Cl ; 2a, 3a : R = H ; 1b, 2b, 3b : R = R'= tBu ; 1c, 2c, 3c : R = R' = allyl .

Scheme 1. Synthesis of phosphine–boranes **3a–c**.




Scheme 3. Synthesis of t-butyldisilylphosphine–borane **4a**.

tion of dimethyl sulphide borane with phosphines **2a–c** at −20°C, followed by warming the solution to 25°C (Scheme 1).

In the case of **2c**, a correct 1:1 stoichiometric ratio of reactants is essential to avoid hydroboration of the allyl function. In these conditions, only complexation is observed. Removal in vacuo of free dimethyl sulphide and solvent in each case gives the crude product as a clean viscous oil. Phosphine–boranes **3a, b** were purified by trap-to-trap distillation, giving white crystalline solids. No decomposition or decomplexation was observed during this process. Attempts to purify **3c** by the same procedure led to an intramolecular regioselective anti-Markovnikov hydroboration reaction giving the cyclic phosphine–borane **3d** as a viscous oil. The same reaction was observed on heating **3c** in a toluene solution at 30°C (Scheme 2).

We also prepared the disilyl derivative **4a** by reaction of n-butyllithium with the phosphine–borane **3a** in the presence of chlorotrimethylsilane (Scheme 3). It exhibits a lower stability than the monosilyl precursor **3a** and its thermal decomposition during purification prevented to use it as a starting material.

Selected NMR data for **3a–d** are collected in Table 1. As expected, the $^{31}P$ chemical shifts of phosphine–borane **3** are downfield compared with the values observed for the free phosphines (compounds **2**) and the $^{1}J_{PH}$ coupling constants are larger for the former ($\Delta^{1}J_{PH} \approx 150$ Hz). For example, for **3d** the $^{11}B$ NMR data (29.5 ppm, td, $^{1}J_{BH} = 101$ Hz, $^{1}J_{BP} = 34$ Hz) suggest four-coordinate boron [10]. In the $^{1}H$ NMR spectrum, the $BH_2$ function gives rise to a broad 1:1:1 triplet at 0.91 ppm and the P–H unit to a doublet at 3.91 ppm. Phosphine–boranes **3a–d** were also characterized by $^{13}C$ NMR spectroscopy and high-resolution mass spectrometry (HRMS).

Flash vacuum thermolysis (FVT) coupled with mass spectrometry (MS) is ideally suited for the characterization of highly reactive species [11]. Thermolysis of **3a, b, d** was carried out in an oven coupled with a high-resolution mass spectrometer as described previously [11b]. The decompositions of the phosphine–boranes were monitored while increasing the temperature. The reactive species produced by FVT were characterized by real-time analysis of the gas flow. Under these conditions, both **3a** and **3b** produce a mirror on the internal surface of the oven above 300°C. The only volatile products which could be detected are isobutene, the free phosphines **2a** or **2b**, and $BH_3$, indicating that $\beta$-elimination which occurred in the thermal process is accompanied by weak decomplexation. We believe that the expected $[H_2B–PH_2]$ intermediate is probably too unstable to be preserved at the temperature of the $\beta$-elimination. Further decomposition (loss of dihydrogen) and formation of boron phosphide layers are likely. So far we have not analysed the structure of this layer.


Scheme 2. Regioselective intramolecular hydroboration of **3c**.

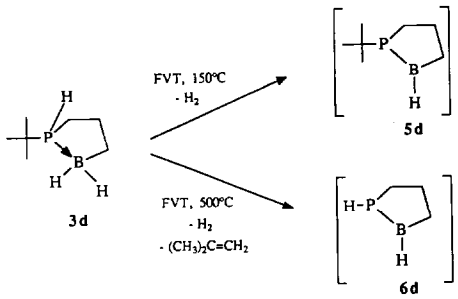
When FVT of **3d** is undertaken, no decomplexation is observed whatever the temperature (150–500°C). At a temperature as low as 150°C, the transient t-butylphosphaborolane **5d** is detected (loss of a molecule of hydrogen ($m/z = 142$)) and characterized by HRMS (calculated for $C_7H_{16}{}^{11}BP$, 142.1082; found, 142.1081). On increasing the temperature (500°C), the elusive phosphaborolane **6d** ($m/z = 86$) is formed by reductive elimination of dihydrogen and $\beta$-elimination of isobutene, as confirmed by HRMS (calculated for $C_3H_8{}^{11}BP$, 86.04567; found, 86.0461) (Scheme 4).

This is the first direct spectrometric evidence of the formation of an unhindered phosphaborolane bearing a protic and hydridic hydrogen within the same molecule. In order to obtain more spectroscopic data on this intermediate, products were analysed at 77 K using a tandem FVT/IR device [11c]. The bands corre-

Table 1
Selected NMR data and boiling points of phosphine–boranes **3a–d**

| Compound | $\delta^{1}H$ [a] | $\delta_{^{31}P}$ ($^{1}J_{PH}$) [a] | $^{1}J_{^{11}B^{31}P}$ | $\delta_{^{11}B}$ [a] ($^{1}J_{^{11}B^{1}H}$) | B.p.(°C) |
|---|---|---|---|---|---|
| **3a** | 0.84 ($BH_3$) | −9.8 (350) | 32 | −44.3 | 60 (2.5 mmHg) |
| | 4.21 (P–H) | | | (101) | |
| **3b** | 0.95 ($BH_3$) | 48.3 (352) | 47 | −42.3 | 100 (2.5 mmHg) |
| | 3.70 (P–H) | | | (98) | |
| **3c** | 0.78 ($BH_3$) | 25.2 (372) | 48.5 | −43.3 | |
| | 4.35 (P–H) | | | (97) | |
| **3d** | 0.91 ($BH_2$) | 27.3 (347) | 33 | −29.5 | 100 (0.05 mmHg) |
| | 3.91 (P–H) | | | (101) | |

[a] $C_6D_6$, 25°C, TMS.




Scheme 4. FVT of **3d**: detection of transient phosphaborolanes **5d** and **6d**.

sponding to the starting material ($\nu_{BH} = 2360$ cm$^{-1}$, $\nu_{PH} = 2240$ cm$^{-1}$, $\nu_{PB} = 1350$ cm$^{-1}$) decreased as the temperature increased, but no other well defined structure with P–H and B–H bonds was observed at higher temperature. These results indicate that **5d** and **6d** probably polymerize on the KBr window even at 77 K.

## 3. Conclusion

A stable cyclic phosphine–borane adduct (**3d**) is efficiently formed by a chemoselective complexation of allyl-t-butylphosphine with $BH_3$ followed by an intramolecular anti-Markovnikov hydroboration of the adduct. This compound leads by thermal dehydrogenation and $\beta$-elimination of isobutene under FVT conditions to the first –PH–BH– structure, stable in the gas phase up to 500°C, but undergoing self-condensation in the condensed phase even at 77 K.

## 4. Experimental

All reactions were carried out under dinitrogen by using standard inert atmosphere and Schlenk techniques. THF, tetraglyme and pentane were distilled from Na/benzophenone under dinitrogen. $^1$H, $^{13}$C, $^{31}$P and $^{11}$B NMR spectra were recorded on a Bruker AM 300 or a Bruker AC 300 spectrometer. Mass spectra were obtained on a Varian MAT 311 instrument.

### 4.1. Synthesis of t-butylchlorophosphines (1a–c)

Mono- and di-t-butylchlorophosphines (**1a** and **1b**) were prepared according to a literature method [7]. Allyl-t-butylchlorophosphine (**1c**) was prepared by slow addition of allylmagnesium chloride (36.3 mmol) to 4.8 g (30.2 mmol) of t-butyldichloro phosphine (**1a**) dissolved in 200 ml of dried THF at −45°C. The mixture was allowed to reach room temperature. Pentane was added and salts were eliminated by filtration. Solvents were removed under vacuum. The product was purified by distillation at 45°C at 4 mmHg (71%). $^{31}$P NMR ($CDCl_3$): $\delta$ 122.9 $^1$H NMR ($CDCl_3$): $\delta$ 1.08 (d, $^3J_{PH} = 13$ Hz), 2.52 (m), 5.15 (m), 5.84 (m). $^{13}$C NMR ($CDCl_3$): $\delta$ 25.4 (qdm, $^1J_{CH} = 127$ Hz, $^2J_{CP} = 17$ Hz), 32.9 (dm, $^1J_{CP} = 31$ Hz), 35.9 (tdm, $^1J_{CH} = 135$ Hz, $^1J_{CP} = 36$ Hz), 118.4 (tdm, $^1J_{CH} = 156$ Hz, $^3J_{CP} = 10$ Hz), 131.9 (ddm, $^1H_{CH} = 156$ Hz, $^2J_{CP} = 10$ Hz).

### 4.2. Reduction of t-butylchlorophosphines 1a–c

*Synthesis of mono- and di-t-butylphosphines (2a,2b)*

Mono- and di-t-butylphosphines (**2a** and **2b**) were prepared according to the literature method except that the reduction was performed in tetraglyme at room temperature for 90 min. The reaction mixture was then placed under vacuum and the phosphines formed were separated from the excess of $LiAlH_4$ and the tetraglyme by trap-to-trap distillation. The yield improved from ca. 40–60% to 65–70%.

**2a**: $^{31}$P NMR ($CDCl_3$) $\delta$: −78 (tm $^1J_{PH} = 191$ Hz). $^1$H NMR ($CDCl_3$): $\delta$ 1.16 (d, $^3J_{PH} = 12$ Hz), 2.82 (d, $^1J_{PH} = 191$ Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 25.9 (dm, $^1J_{CP} = 2.7$ Hz), 32.9 (qdm, $^1J_{CH} = 125$ Hz, $^2J_{CP} = 11$ Hz).

**2b**: $^{31}$P NMR ($CDCl_3$) $\delta$: 20.6 (d, $^1J_{PH} = 193$ Hz). $^1$H NMR ($CDCl_3$): $\delta$ 1.21 (d, $^3J_{PH} = 11.4$ Hz), 3.21 (d, $^1J_{PH} = 193$ Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 32.1 (d, $^2J_{PC} = 13.4$ Hz).

*Synthesis of allyl-t-butylphosphine (2c)*

Allyl-t-butylphosphine (**2c**) was prepared by reduction of the corresponding chlorophosphine using $AlHCl_2$ [9] as a chemoselective reducing agent.

Allyl-t-butylchlorophosphine (**1c**) (18.3 mmol) dissolved in 3 ml of tetraglyme was slowly added to the reducing mixture ($LiAlH_4$, 0.264 g, 6.96 mmol, and $AlCl_3$, 2.82 g, 21.2 mmol, in 60 ml of tetraglyme at −20°C). The reaction was allowed to reach room temperature and left at this temperature for 90 min. The mixture was then placed under vacuum and allyl-t-butylphosphine (**2c**) was obtained after purification by trap-to-trap distillation and obtained in a ca. 85% yield. $^{31}$P NMR ($CDCl_3$) $\delta$: −23.1 (d, $^1J_{PH} = 167$ Hz). $^1$H NMR ($CDCl_3$): $\delta$ 1.15 (d, $^3J_{PH} = 11.8$ Hz), 2.40 (m), 5.10 (m), 5.80 (m). $^{13}$C NMR ($CDCl_3$): $\delta$ 23.4 (tdm, $^1J_{CH} = 128$ Hz, $^1J_{CP} = 15$ Hz), 27.3 (dm, $^1J_{CP} = 9$ Hz), 30.0 (qdm, $^1J_{CH} = 126$ Hz, $^2J_{CP} = 12$ Hz), 115.7 (tdm, $^1J_{CH} = 156$ Hz, $^3J_{CP} = 9$ Hz), 135.5 (ddm, $^1J_{CH} = 154$ Hz, $^2J_{CP} = 7$ Hz).

### 4.3. Complexation of t-butylphosphines (2a–c)

Dimethyl sulphide–borane (10.5 mmol) was slowly added to the phosphines **2a–c** (10 mmol) dissolved in 15 ml of THF cooled to −20°C. The reaction mixture was allowed to reach room temperature. The crude product was obtained in essentially quantitative yield.

Purification of **3a–b** was performed by distillation under vacuum; **3c** was characterized as a crude product.

**3a**: b.p. = 60°C (2.5 mmHg). $^{31}$P NMR ($C_6D_6$) $\delta$: −9.5 (tq $^1J_{PH}$ = 350 Hz, $^1J_{PB}$ = 32 Hz). $^1$H NMR ($C_6D_6$): $\delta$ 0.84 (q, $^1J_{BH}$ = 102 Hz), 1.08 (d, $^3J_{PH}$ = 15 Hz, 4.21 (dq, $^1J_{PH}$ = 350 Hz, $^3J_{HH}$ = 7.6 Hz). $^{13}$C NMR ($C_6D_6$): $\delta$ 25.5 (dm, $^1J_{CP}$ = 35 Hz), 27.9 (qdm, $^1J_{CH}$ = 128 Hz, $^2J_{CP}$ = 24 Hz). $^{11}$B NMR ($C_6D_6$): $\delta$ −44.3 (dq, $^1J_{BH}$ = 101 Hz, $^1J_{BP}$ = 32 Hz). IR (film) $\nu$ = 2360 ($BH_3$), 2240 (PH), 1350 cm$^{-1}$ (B–P). HRMS: [M − H·]$^+$ calc. 103.0848, found 103.0854. Analysis Found: C 45.87; P 29.53, B 10.32. $C_4H_{14}BP$ calc.: C, 46.24, P 29.86, B 10.40%.

**3b**: b.p. = 100°C (2.5 mmHg). $^{31}$P NMR ($C_6D_6$) $\delta$: 48.3 (dq $^1J_{PH}$ = 352 Hz, $^1J_{PB}$ = 47 Hz). $^1$H NMR ($C_6D_6$): $\delta$ 0.93 (d, $^3J_{PH}$ = 13 Hz), 0.95 (q, $^1J_{BH}$ = 98 Hz), 3.70 (dq, $^1J_{PH}$ = 350 Hz, $^3J_{HH}$ = 6.6 Hz). $^{13}$C NMR ($C_6D_6$): $\delta$ 29.1 (qdm, $^1J_{CH}$ = 128 Hz, $^2J_{CP}$ = 2 Hz, 30.6 (dm, $^1J_{CP}$ = 27 Hz). $^{11}$B NMR ($C_6D_6$): $\delta$ −42.3 (dq, $^1J_{BH}$ = 98 Hz, $^1J_{BP}$ = 47 Hz). IR (film) $\nu$ = 2360 ($BH_3$), 2240 (PH), 1350 cm$^{-1}$ (B–P). Analysis Found: C 59.36, P 18.83, B 6.44. $C_8H_{22}BP$ calc.: C 60.06, P 19.39, B 6.75%.

**3c** (crude product): $^{31}$P NMR ($C_6D_6$) $\delta$: 25.2 (dqm, $^1J_{PH}$ = 372 Hz, $^1J_{PB}$ = 48.5 Hz). $^{11}$B NMR ($C_6D_6$): $\delta$ −43.3 (dq, $^1J_{BH}$ = 97 Hz, $^1J_{BP}$ = 48.5 Hz). IR (film) $\nu$ = 2360 ($BH_3$), 2240 (PH), 1350 cm$^{-1}$ (B–P). During the distillation process, we observed the formation of the corresponding cyclic phosphine–borane **3d** by an intramolecular hydroboration of the allylic double bond.

**3d**: b.p. = 100°C (0.05 mmHg). $^{31}$P NMR ($C_6D_6$) $\delta$: 27.3 (dq, $^1J_{PH}$ = 344 Hz, $^1J_{PB}$ = 33 Hz). $^{11}$B NMR ($C_6D_6$): $\delta$ −29.5 (td, $^1J_{BH}$ = 101 Hz, $^1J_{BP}$ = 34 Hz). $^1$H NMR ($C_6D_6$): $\delta$ 0.82 (d, $^3J_{PH}$ = 14 Hz), 1.23–1.84 (m complex), 3.91 (dm, $^1J_{PH}$ = 344 Hz). $^{13}$C NMR ($C_6D_6$): $\delta$ 18.7 (td, $^1J_{CH}$ = 132 Hz, $^1J_{CP}$ = 36 Hz, 26.2 (d, $^1J_{CP}$ = 30 Hz, 27 (qd, $^1J_{CH}$ = 127 Hz, $^2J_{CP}$ = 2.5 Hz, 28.7 (td, $^1J_{CH}$ = 130 Hz, $^2J_{CP}$ = 19 Hz). IR (film) $\nu$ = 2360 ($BH_3$), 2240 (PH), 1350 cm$^{-1}$ (B–P). HRMS: [M-H·]$^+$ calc. 143.1160, found 143.1150. Decomposition of **3d** was observed during the analysis.

### 4.4. Silylation of phosphine–borane 3b

Disilylation of phosphine **3a** was performed by slow addition of n-butyllithium (2 equivalents, 14.4 mmol) to phosphine **3a** (7 mmol) in 10 ml of THF at −90°C. The reaction was left for 10 min at this temperature and chlorotrimethylsilane (16.8 mmol) was added. The mixture was then allowed to reach room temperature. After addition of pentane and elimination of salts and solvents the product was distilled under vacuum. However, it decomposed during this process. The NMR analysis was performed on the crude product. $^{31}$P NMR ($C_6D_6$): $\delta$ −72.1 (q, $^1J_{PB}$ = 31 Hz). $^1$H NMR ($C_6D_6$): $\delta$ 0.13 (d, $^3J_{PH}$ = 5 Hz), 1.03 (d, $^3J_{PH}$ = 14 Hz). $^{11}$B NMR ($C_6D_6$): $\delta$ −42.4 (qd, $^1J_{BH}$ = 101 Hz, $^1J_{BP}$ = 31 Hz).

### 4.5. Pyrolysis studies

For FVT of phosphine–borane **3d**, thermolysis was performed at various temperatures between 150 and 500°C under $10^{-4}$ hPa (oven dimensions: length = 10 cm, i.d. = 14 mm). The oven was coupled either to an IR cryostat, allowing direct recording of spectra under vacuum at 77 K, or to a high-resolution mass spectrometer. At 150°C, the transient t-butylphophaborolane **5d** formed by loss of a molecule of $H_2$ was characterized by real-time MS analysis. At a higher temperature (500°C), the elusive phosphaborolane **6d**, formed by reductive elimination of dihydrogen followed by $\beta$-elimination of isobutene, was characterized by real-time MS analysis; the isobutene elimination was shown not to occur in the ion source of the mass spectrometer. **5d** HRMS: $C_7H_{16}P^{11}B$ calc. 142.1082, found 142.1081. **6d** HRMS: $C_7H_{16}P^{11}B$ calc. 86.04567, found 86.0461.

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