

Synthesis and structure of cyclic phosphine–boranes

Hubert Schmidbaur ^{*}, Marcus Sigl, Annette Schier

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Abstract

In a search for cyclic phosphine–boranes, which can be expected to undergo ring opening polymerisation, or decomposition, to leave boron phosphide, the hydroboration reaction of ω -alkenyl-diphenylphosphines with boranes was investigated. Addition of one equivalent of borane (introduced as its tetrahydrofuran adduct) to phosphines $H_2C=CH-(CH_2)_n-PPh_2$ ($n = 0, 1, 2$) gave the corresponding phosphine–boranes $H_2C=CH-(CH_2)_n-PPh_2BH_3$ without any further cyclisation. With an excess of $(thf)BH_3$, hydroboration of the olefinic function occurred, but again no ring closure. Treatment of the alkenylphosphines with 9-borabicyclononane gave the expected cyclic phosphine–boranes $(C_8H_{14})B-(CH_2)_n-PPh_2$ ($n = 3, 4$) in good yield as crystalline products. The structures of the two heterocycles have been determined by X-ray diffraction methods. They show the expected strain-free ring systems with short P–B bonds, comparable with the isoelectronic Si–C systems.

Keywords: Phosphine–boranes; Hydroboration; Alkenylphosphines; Borabicyclononane; 1,2-Boraphosphacycloalkanes

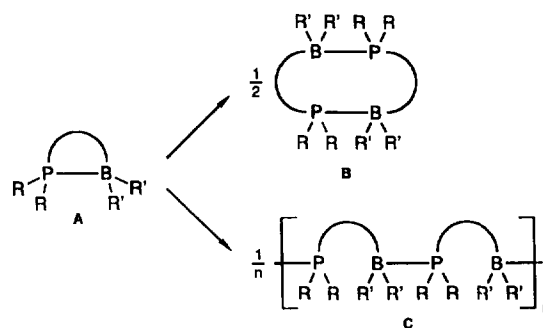
1. Introduction

Phosphine–boranes of the general formula R_3P-BH_3 are an intriguing class of compounds [1]. It has already been noted in the earliest studies that the P–B donor–acceptor bond is unusually strong and that the B–H bonds appear to show signs of an ‘Umpolung’ [2]. The adducts of tertiary phosphines with monoborane BH_3 are stable to oxidation and hydrolysis even in strongly acidic media. Concentrated nitric acid is required for a total destruction of the compounds.

These properties are modified in derivatives with different numbers and types of substituents at phosphorus and/or boron ($R_3P-BH_mR'_{3-m}$), and generally more reactive species are obtained. These were found to have extensive synthetic potential in organic chemistry, and a large number of very useful preparations have been developed with phosphine–boranes as key reagents [3]. The role of phosphine–boranes as ligands in inorganic and organometallic chemistry is more limited, but is currently attracting growing interest [4].

The present study was initiated in order to provide access to cyclic phosphine–boranes, which in the past were considered only sporadically [5–8]. Heterocycles of this type (A) can be expected to be stable regarding

the underlying P–B bond (above), but these bonds may also re-form in thermal ring polymerisation reactions to give large ring oligomers or polymers (B, C). More drastic thermolysis could lead to boron phosphides $(BP)_n$, provided that the organic components of the heterocycle or polymer are lost in an efficient process of elimination of olefins and other hydrocarbons.

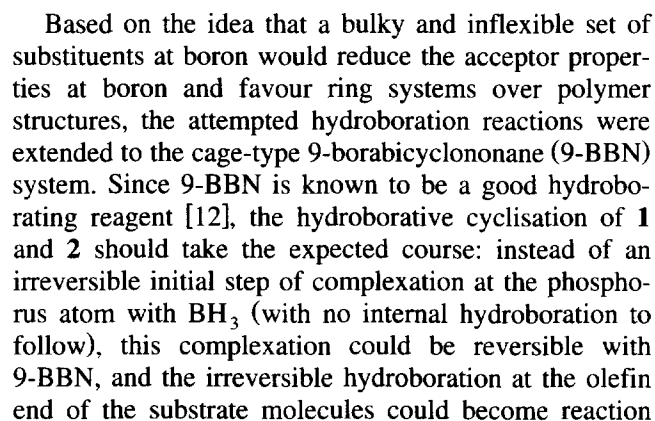


2. Results

The most promising general synthetic concept for the formation of phosphine–borane heterocycles is offered

^{*} Corresponding author.

Treatment of compound **5** with an excess of (thf)BH₃ led only to the formation of the hydroboration product (**7**), with one equivalent of BH₃ added (anti-Markovnikov) to the terminal double bond of the 3-butenyl group (Eq. (1)). Addition of additional BH₃ (from (thf)BH₃) is clearly preferred over internal hydroboration (from the -PPh₂BH₃ group in **5**).



Crystals of compound **8** (from diethyl ether) are orthorhombic, space group $Pna2_1$ with $Z = 4$ formula units in the unit cell. The molecules show no unusual intermolecular interactions. The five-membered ring is in an envelope conformation, with the middle carbon atom (C10, Fig. 1) out of the plane of the other four ring atoms. The P–B bond length of 2.072(3) Å is longer than comparable parameters of open-chain phosphine–boranes, suggesting a weakening of this bond through conformational strain. The ring C–C bonds have standard single bond distances (C9–C10 1.520(4) Å, C10–C11 1.541(4) Å), and the C–B bond (C11–B 1.628(4) Å) is not unusual for tetracoordinate boron atoms. It thus appears that the ring system of compound **8** is slightly strained and the strain is affecting predominantly the P–B donor–acceptor bond. This bond is clearly elongated compared with standard reference data [1] and in the homologous six-membered ring compound (**9**, below).

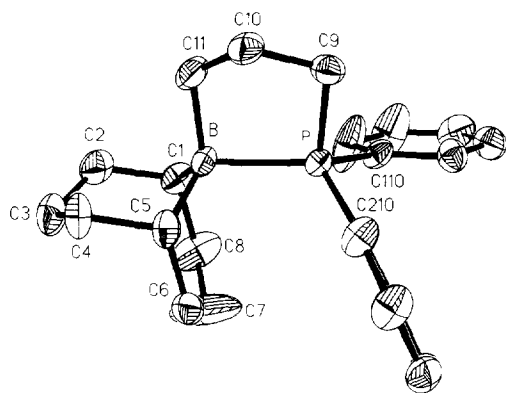


Fig. 1. Molecular structure of compound **8** with atomic numbering (ORTEP; 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg) are as follows: P–B, 2.072(3); P–C9, 1.828(2); P–C110, 1.816(2); P–C210, 1.812(2); C9–C10, 1.520(4); C10–C11, 1.541(4); B–C11, 1.628(4); B–C1, 1.621(3); B–C5, 1.628(4); C1–C2, 1.543(4); C2–C3, 1.521(5); C3–C4, 1.563(4); C4–C5, 1.543(3); C5–C6, 1.543(4); C6–C7, 1.463(5); C7–C8, 1.429(5); C8–C1, 1.530(4); C110–P–C210, 104.6(1); C110–P–C9, 104.9(1); C110–P–B, 123.2(1); C9–P–C210, 106.7(1); C210–P–B, 118.1(1); C9–P–B, 96.9(1); C1–B–C5, 105.6(2); C1–B–C11, 115.4(2); C5–B–C11, 116.5(2); C1–B–P, 117.3(2); C5–B–P, 107.1(2); C11–B–P, 94.8(2); C1–C2–C3, 114.6(2); C2–C3–C4, 113.8(2); C3–C4–C5, 113.4(2); C4–C5–C6, 111.2(2); C5–C6–C7, 117.3(2); C6–C7–C8, 125.0(3); C7–C8–C1, 118.0(3); C8–C1–C2, 112.2(2); P–C9–C10, 106.3(2); C9–C10–C11, 106.7(2); C10–C11–B, 111.8(2).

P–B bonds in phosphine–boranes are generally longer than the bonds in isoelectronic Si–C systems [13]; this is surprising, since with almost equal sums of

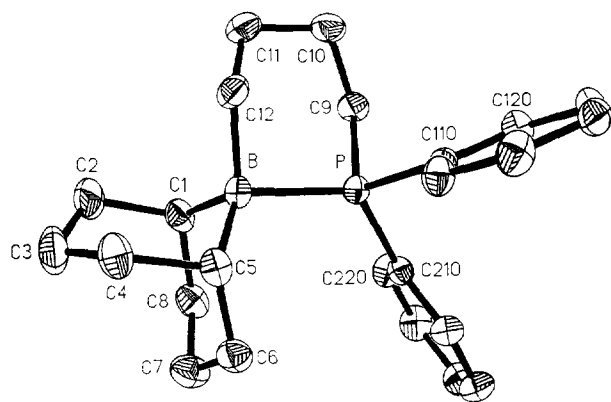
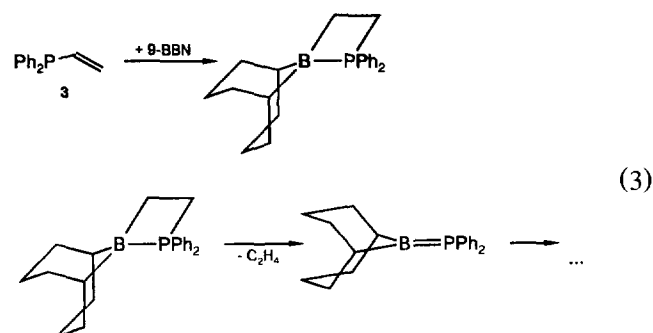


Fig. 2. Molecular structure of compound **9** with atomic numbering (ORTEP; 50% probability ellipsoids). Selected bond lengths (Å) and angles (deg) are as follows: P–B, 2.029(2); P–C9, 1.824(1); P–C110, 1.821(1); P–C210, 1.826(1); C9–C10, 1.530(2); C10–C11, 1.524(2); C11–C12, 1.535(2); B–C12, 1.643(2); B–C1, 1.632(2); B–C5, 1.625(2); C1–C2, 1.542(2); C2–C3, 1.535(2); C3–C4, 1.533(2); C4–C5, 1.547(2); C5–C6, 1.531(2); C6–C7, 1.532(2); C7–C8, 1.534(2); C8–C1, 1.539(2); C110–P–C210, 102.24(6); C110–P–C9, 104.51(7); C110–P–B, 115.67(6); C9–P–C210, 104.23(7); C210–P–B, 125.17(6); C9–P–B, 102.90(7); C1–B–C5, 104.9(1); C1–B–C12, 114.7(1); C5–B–C12, 115.0(1); C1–B–P, 108.5(1); C5–B–P, 115.7(1); C12–B–P, 98.22(9); C1–C2–C3, 114.0(1); C2–C3–C4, 114.9(1); C3–C4–C5, 116.0(1); C4–C5–C6, 112.8(1); C5–C6–C7, 114.7(1); C6–C7–C8, 114.8(1); C7–C8–C1, 116.3(1); C8–C1–C2, 112.4(1); P–C9–C10, 111.8(1); C9–C10–C11, 113.9(1); C10–C11–C12, 113.4(1); C11–C12–B, 117.7(1).

the covalent radii (P–B vs. Si–C) the formal charges at the phosphorus and carbon atoms could mean a strengthening (and shortening) of the $(^+)P-B(^-)$ linkage. Obviously, contributions from such ‘semipolar double bonds’ appear to be small, or at least do not show in the structural parameters.

Crystals of compound **9** are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units per unit cell. There are no unusual intermolecular contacts in the lattice. The six-membered ring has a chair conformation (Fig. 2) with the B- and P-bonded carbon atoms (C12, C9) above and below the plane of the atoms B, P, C10, C11. The P–B bond (2.029(2) Å) is shorter than in the lower homologue **8**, while the endocyclic B–C bond (B–C12 1.643(3) Å) is longer than the corresponding bond in **8**. The ring C–C bonds show no such anomalies.

The reaction of 9-BBN with diphenyl(vinyl)phosphine did not produce the expected boraphosphetane. The ^{31}P NMR spectrum of the reaction mixture (in thf) showed peaks at $\delta = 36$ and 7.6 ppm, which could be assigned to phosphine–boranes of various ring sizes, but attempts to isolate the products met with failure owing to extensive decomposition (Eq. (3)).



The observed low-field shift of the ^{31}P NMR signals of the decomposed material could arise from phosphino–boranes generated by loss of olefin from the boraphosphetane intermediate [14].

3. Experimental

3.1. General

All experiments were carried out routinely in an atmosphere of purified dry nitrogen. Solvents were dried and kept under nitrogen, and glassware was oven-dried and filled with nitrogen. Starting materials were either commercially available or were prepared following literature methods.

3.2. Allyl(diphenyl)phosphine–borane, **4**

A solution of allyl(diphenyl)phosphine (**1**, 0.57 g, 2.5 mmol) in thf (3 ml) is treated with 2.5 ml of a 1 M

solution of $(C_4H_8O)BH_3$ in thf. After 1 h at 20°C the solvent is removed from the reaction mixture in a vacuum. The residue is washed twice with pentane to remove unreacted phosphine. Yield 0.51 g (85%), colourless oil. 1H NMR ($CDCl_3$, 23°C): δ = 3.06, dd, $J(P,H)$ = 13 Hz, $J(H,H)$ = 7 Hz, 2H, PCH_2 ; 5.08, m, 2H, $CH_2=C$; 5.78, m, 1H, $CCHC$; 7.45–7.67, m, 10H, Ph. $^{11}B\{^1H\}$ NMR (v.s.): δ = –39.6, d, $J(P,B)$ = 49 Hz. $^{31}P\{^1H\}$ NMR (v.s.): δ = 15.9, br s. $^{13}C\{^1H\}$ NMR (v.s.): δ = 31.8, d, $J(P,C)$ = 35 Hz, PCH_2 ; 120.3, d, $J(P,C)$ = 11 Hz, CCH_2 ; 128.2, d, $J(P,C)$ = 6 Hz, CH; 128.6 (10), 128.7 (55), 131.2 (3), 132.3 (8) for $\delta(J)$ of *meta*-, *ipso*-, *para*-, and *ortho*-Ph carbon atoms. MS (EI): m/z = 226, $M - BH_3$; 183, $M - BH_3 - C_3H_6$. Anal. Found: C, 74.58; H, 7.92. $C_{15}H_{18}BP$ (240.09). Calc.: C, 75.04; H, 7.56%.

3.3. 3-Butenyl(diphenyl)phosphine–borane, 5

As described for **4**, with 3-butenyl(diphenyl)phosphine (**2**, 1.06 g, 4.16 mmol) and 4.2 ml of 1 M (thf) BH_3 in thf solution (10 ml). Yield 0.98 g (85%), colourless oil. 1H NMR (v.s.): δ = 2.20, m, 2H, $PCCH_2$; 2.37, dt, $J(P,H)$ = 11 Hz, $J(H,H)$ = 7 Hz, 2H, PCH_2 ; 4.80, m, 2H, $CH_2=C$; 5.62, m, 1H, CH. $^{11}B\{^1H\}$ NMR (v.s.): δ = –40.2, d, $J(P,B)$ = 52 Hz. $^{31}P\{^1H\}$ NMR (v.s.): δ = 16.4, br s. MS (EI): m/z = 239, $M - BH_3$; 183, $M - BH_3 - C_4H_8$. Anal. Found: C, 75.33; H, 7.74. $C_{16}H_{20}BP$ (254.12). Calc.: C, 75.63; H, 7.93%.

3.4. Diphenyl(vinyl)phosphine–borane, 6

This compound was prepared from phosphine **3** and (thf) BH_3 . It has been fully characterised in previous studies [3].

3.5. 3-Boranylbutyl(diphenyl)phosphine–borane(thf), 7

Compound **5** (1.06 g, 4.16 mmol) is dissolved in thf (10 ml) and treated at –50°C with 4.2 ml of a 1 M solution of (thf) BH_3 . The reaction mixture is allowed to warm to room temperature over a period of 2 h, and the solvent is removed in a vacuum. The residue is dissolved in dichloromethane and precipitated by addition of pentane. Yield 0.66 g (47%), colourless oil, b.p. 135°C/0.05 Torr. 1H NMR ($CDCl_3$, 23°C): δ = 2.20, br s, 2H, PCH_2 ; 7.42–7.66, m, 10H, Ph; 3.64, m, 4H, OCH_2 ; 0.9–1.8, m, 10H. $^{11}B\{^1H\}$ NMR (v.s.): δ = –40.1, br s, BH_3 ; 19.0, br s, BH_2R . $^{31}P\{^1H\}$ NMR (v.s.): δ = 15.7, br s. MS (EI): m/z = 253, $M - BH_3 - thf$; 183, $M - BH_3 - thf - C_4H_8$. Anal. Found: C, 69.97; H, 9.75. $C_{16}H_{23}B_2P \cdot C_4H_8O$ (340.08). Calc.: C, 70.64; H, 9.20%.

3.6. cyclo-[(9-Borabicyclo[3.3.1]nonanyl)propyl(diphenyl)phosphine], 8

9-BBN (4.7 ml of 0.5 M thf solution) was added to a solution of allyl (diphenyl) phosphine (**1**, 0.53 g, 2.34 mmol) in 5 ml of thf. After refluxing for 1 h the solvent was removed under reduced pressure and the product was recrystallised from diethyl ether. Yield 0.75 g (93%) colourless crystals, m.p. 115°C. 1H NMR (CD_2Cl_2 , 23°C): δ = 1.06, br m, 4H, CH_2CH_2B ; 1.4–2.0, m, 14H, 9-BBN–H; 2.36, dt, $J(P,H)$ = 17 Hz, $J(H,H)$ = 7 Hz, 2H, PCH_2 ; 7.43–7.59, m, 10H, Ph. $^{11}B\{^1H\}$ NMR (v.s.): δ = 0.0, br s. $^{31}P\{^1H\}$ NMR (v.s.): δ = 10.3, br s. $^{13}C\{^1H\}$ NMR (v.s.): δ = 23.7, br s, 9-BBN– C^α ; 24.8, s, 9-BBN– C^γ ; 33.0, s, 9-BBN– C^β ; 33.1, s, 9-BBN– C^b ; 24.1, d, $J(P,C)$ = 17 Hz, PCH_2CH_2 ; 26.5, br s, BCH_2 ; 32.1, d, $J(P,C)$ = 38 Hz, PCH_2 ; 129.0 (8), 130.7 (2), 132.8 (34), 133.7 (9) for $\delta(J)$ of *meta*-, *para*-, *ipso*- and *ortho*-Ph carbon atoms. MS (EI): m/z = 348, M ; 239, $M + 1 - C_8H_{14}$. Anal. Found: C, 78.66; H, 8.85. $C_{23}H_{30}BP$ (348.28). Calc.: C, 79.32; H, 8.68%.

3.7. cyclo-[(9-Borabicyclo[3.3.1]nonanyl)butyl(diphenyl)phosphine], 9

As described for **8**, with 3-butenyl(diphenyl)phosphine (**2**, 0.94 g, 3.91 mmol) and 7.9 ml of 0.5 M 9-BBN in thf solution (10 ml). Yield 1.23 g (87%) colourless crystals, m.p. 140°C. 1H NMR (CD_2Cl_2 , 23°C): δ = 1.0–1.3, m, 6H, $CH_2CH_2CH_2B$; 1.4–2.0, m, 14H, 9-BBN–H; 2.39, m, 2H, PCH_2 ; 7.37–7.52, m, 10H, Ph. $^{11}B\{^1H\}$ NMR (v.s.): δ = –5.0, br s. $^{31}P\{^1H\}$ NMR (v.s.): δ = –1.8, br s. $^{13}C\{^1H\}$ NMR (v.s.): δ = 24.3, br s, 9-BBN– C^α ; 24.9, s, 9-BBN– C^γ ; 33.2, br s, 9-BBN– C^β ; 22.0, br s, BCH_2 ; 22.0, d, $J(P,C)$ = 27 Hz, PCH_2 ; 23.9, d, $J(P,C)$ = 2 Hz, CH_2CH_2B ; 25.0, d, $J(P,C)$ = 4 Hz, PCH_2CH_2 ; 128.6 (8), 130.1 (3), 133.0 (9), 133.6 (33) for $\delta(J)$ of *meta*-, *para*-, *ortho*- and *ipso*-Ph carbon atoms. MS (EI): m/z = 363, $M + 1$; 253, $M + 1 - C_8H_{14}$. Anal. Found: C, 79.39; H, 9.03; P, 8.27. $C_{24}H_{32}BP$ (362.30). Calc.: C, 79.56; H, 8.90; P, 8.55%.

3.8. Crystal structure determinations

Suitable single crystals of **8** and **9** were sealed in glass capillaries and used for measurement of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Diffraction intensities were corrected for Lorentz and polarisation effects but not for absorption. The structures were solved by direct methods and refined by full matrix least squares calculations against F^2 . The thermal motion of all non-hydrogen atoms was

Table 1
Crystal data, data collection, and structure refinement for compounds **8** and **9**

	8	9
<i>Crystal data</i>		
Formula	C ₂₃ H ₃₀ BP	C ₂₄ H ₃₂ BP
M _r	348.25	362.28
Crystal system	orthorhombic	triclinic
Space group	<i>Pna</i> 2 ₁ (No. 33)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> (Å)	8.619(1)	9.116(1)
<i>b</i> (Å)	15.352(1)	9.735(1)
<i>c</i> (Å)	14.674(1)	12.831(1)
α (deg)	90	69.28(1)
β (deg)	90	86.99(1)
γ (deg)	90	71.36(1)
<i>V</i> (Å ³)	1941.6(3)	1006.8(2)
ρ_{calc} (g cm ⁻³)	1.191	1.195
<i>Z</i>	4	2
<i>F</i> (000) (e)	752	392
μ (Mo K α) (cm ⁻¹)	1.44	1.42
<i>Data collection</i>		
Diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
Radiation	Mo K α , 0.71069 Å	Mo K α , 0.71069 Å
<i>T</i> (°C)	–62	–68
Scan mode	ω – θ	ω – θ
<i>hkl</i> range	+10/–19/±18	±11/±11/±15
$\sin(\theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.64	0.62
Measured refl.	4024	3696
Unique refl.	4024	3691
Observed refl.	3681	3371
<i>I</i> ≥	2 σ <i>I</i>	2 σ <i>I</i>
<i>Refinement</i>		
Refined parameters	225	235
H atoms (found/calc.)	0/30	0/32
<i>R</i> 1 ^a	0.0422	0.0331
<i>wR</i> 2 ^b	0.1064	0.0830
(Shift/error) _{max}	0.000	0.000
ρ_{fin} (max/min) (e Å ⁻³)	+0.277/–0.259	+0.283/–0.230

^a $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$.

^b $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0592$ (**8**), 0.0377 (**9**); $b = 0.96$ (**8**), 0.46 (**9**).

treated anisotropically. All hydrogen atoms were placed in idealised calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{\text{iso(fix)}} = 1.5U_{\text{eq}}$ of the corresponding C

atom). Further information on crystal data, data collection, and structure refinement are summarised in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions.

Anisotropic thermal parameters, tables of interatomic distances and angles, and tables of observed and calculated structure factors have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 405268, 405269.

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