Temperature-dependent Ring-Opening and -Closure of a Cyclic Phosphane–Borane☆

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A phosphane–borane (**3**) with the P–B bond integrated into a seven-membered ring was prepared from 4-pentenyl-diphenylphosphane (**4**) by hydroboration using 9-borabicyclononane (9-BBN). The product was confirmed to have a ring structure in the solid state by single crystal X-ray diffraction. The P–B distance of 2.057(2) Å is indicative of a standard donor–acceptor bond similar to the type found in homologous five- and six-membered rings. The room-temperature ^{31}P-NMR signal of the compound in various solvents ($\delta \approx -15$) is not compatible with the cyclic structure and suggests that ring opening occurs as the compound is dissolved. Variable-temperature NMR work corroborated this assumption, and the enthalpy of ring closure was determined to be $\Delta H = -30.5(4)$ kJmol^{-1}. In CD_2Cl_2 at −90°C, δ^{31}P is shifted to +3.5 ppm to low field, suggesting virtually complete ring closure under these conditions.

Introduction

Ever since their discovery phosphane–boranes of the type R_3P-BH_3 have attracted considerable interest because of their unexpected chemical properties. The compounds were found to be surprisingly inert towards air and moisture, and proved robust even when treated with strong hot acid and base[1]. A detailed theoretical analysis on various levels of sophistication of the chemical bonding suggested a strongly reduced polarity of the B–H bonds, approaching almost an "Umpolung" from hydridic to protic character of the hydrogen atoms[2].

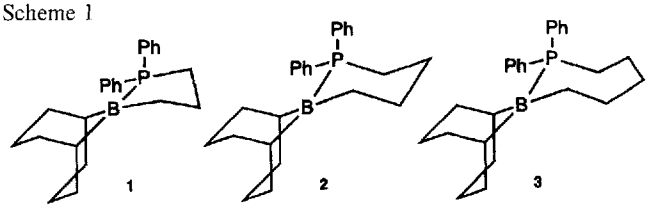
Recent renewed attention paid to phosphane–boranes is associated with the use of the compounds as powerful intermediates in the synthesis of phosphane ligands for homogenous catalysis[3]. The coordination of borane effects both the phosphane protection and the activation of adjacent groups. Furthermore, phosphane–boranes are proposed as precursors for boron phosphide BP, a less common example of a III/V binary system of interest in material science[4].

In this context we have investigated cyclic phosphane–boranes with the P–B bond as an integral part of a heterocycle; these could be expected to undergo reversible polymerization depending on the ring size and the substitution pattern. After the successful preparation of five- and six-membered ring prototypes (**1**, **2**), we have now investigated a seven-membered ring analogue (**3**)[5].

Preparation, Properties and Structure of the Compounds

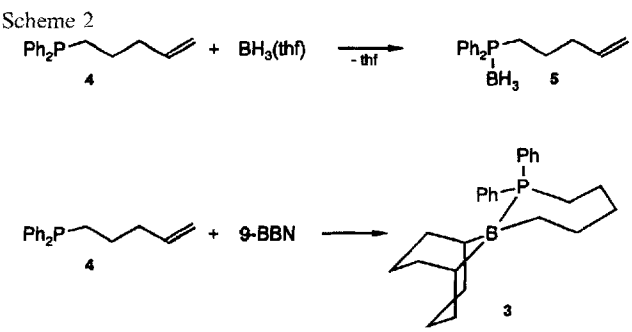
The method of synthesis was adopted from the preparation of **1** and **2**. 5-Bromopentene was treated with potassium diphenylphosphide in tetrahydrofuran at −70°C to give an acceptable yield (76%) of 5-pentenyl-diphenylphosphane (**4**) as a colourless liquid (b.p. 150°C/0.1 Torr)[6]. This compound was found to add one equivalent of borane BH_3 when reacted with (thf)BH_3 at ambient temperature[7]. According to its analytical and spectral data, the product (**5**, m.p. 48°C; 94% yield) is a standard phosphane–borane (see the Experimental Section). All attempts to induce intramolecular hydroboration to give a seven-membered ring with an endocyclic $-Ph_2P-BH_2-$ ring unit failed.

Scheme 1



Hydroboration was successful, however, when compound **4** was refluxed with 9-borabicyclononane (9-BBN) in thf. Compound **3** was obtained in 92% yield as a colourless oil which can be readily crystallized at low temperature (m.p. 10°C). The product is sensitive to air and moisture and is readily soluble in common organic solvents, excluding hydrocarbons.

Scheme 2



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The analytical and spectral data (NMR, MS) are in general agreement with the proposed composition, but surprisingly the ^{31}P-NMR signals of solutions in several solvents ($CDCl_3$, CD_2Cl_2, tetrahydrofuran) were found at high field ($\delta^{31}P = -15$ in $CDCl_3$) in the phosphane region, and were thus close to the signal for the precursor **4** ($\delta^{31}P = -15.9$). The difference observed for the reference compounds (**1**, **2**) between the phosphane and the corresponding phosphane–borane ($\Delta\delta > 12$ ppm) is not reproduced in this case. Moreover, the signals observed for **3** were found to be rather sharp instead of being broadened by quadrupolar interactions as expected for phosphane–boranes with direct P–B bonding. These results are instead compatible with an open-chain compound in which the pentane is terminated by *free* Ph_2P and (BBN) groups (**3b**).

In order to clarify this point, single crystals of compound **3** were grown from the melt and subjected to an X-ray diffraction study. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. At variance with the solution data, the lattice contains independent heterocyclic molecules in a twisted-tub conformation (Figure 1). The endocyclic P–B bond [2.057(2) Å] closely resembles those of the six-membered ring **2** [2.029(2) Å] and the five-membered ring **1** [2.075(3) Å][5]. The two phenyl groups and the BBN cage are in a staggered conformation as projected down the P–B bond (Figure 2). The individual molecules have no crystallographically imposed symmetry. The center of inversion associated with space group $P\bar{1}$ is located between two enantiomeric chiral molecules. The details of the molecular structures show no anomalies.

Figure 1. Molecular structure of compound **3** (**3a**) in the crystal with atomic numbering (ORTEP, 50% probability ellipsoids; H atoms omitted for clarity; only one of the two enantiomers is shown). Selected bond lengths [Å] and angles [°]: P–B 2.057(2), P–C1 1.834(2), P–C111 1.835(2), P–C211 1.821(2), B–C5 1.639(2), B–C6 1.635(2), B–C10 1.629(2). C1–P–B 107.47(7), C111–P–B 121.97(7), C211–P–B 116.66(7), C1–P–C111 102.36(7), C1–P–C211 105.39(7), C111–P–C211 101.16(7), C5–B–P 103.2(1), C6–B–P 108.0(1), C10–B–P, 114.3(1), C5–B–C6 114.7(1), C6–B–C10 104.9(1), C5–B–C10 112.1(1)

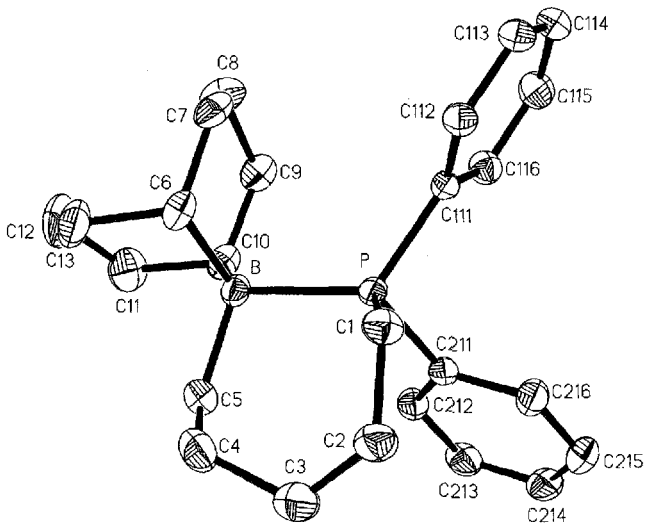
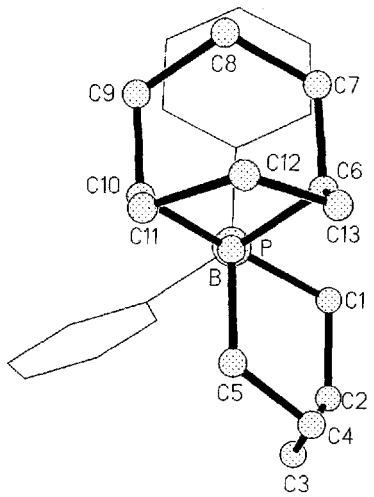


Figure 2. Projection of the structure of molecule **3a** down the P–B axis, showing the staggered conformation (arbitrary radii)

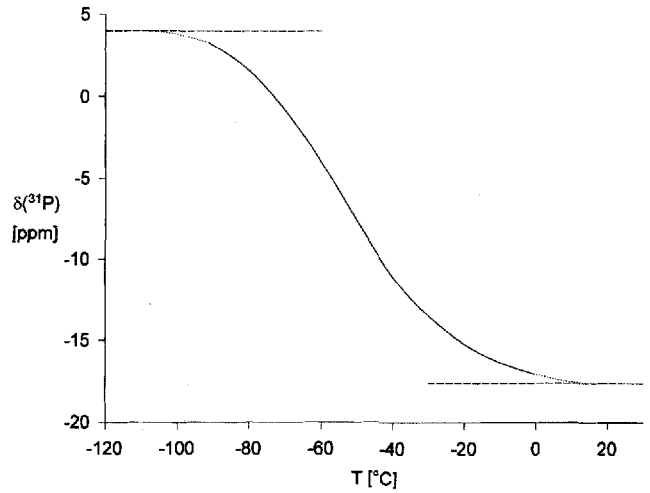


The crystal structure investigation thus proved that compound **3** is indeed a *cyclic* phosphane–borane, at least in the solid state. The "normal" P–B distance does not suggest a very weak bond that could easily be cleaved, for example by solvation. Following recent reports on B–P bond cleavage as observed by dynamic NMR spectroscopy[8], more detailed solution NMR studies were carried out.

Variable Temperature Solution NMR Studies

Dilute dichloromethane solutions of compound **3** show a single sharp $^{31}P\{^1H\}$ resonance at $\delta = -17$ (Figure 3). As the temperature is lowered, this resonance broadens significantly and shifts to lower field, reaching a value of $\delta = +3.3$ at -90 °C. This process is fully reversible with virtually no hysteresis, and similar results are obtained for solutions in trichloromethane (within their more limited temperature region, i.e. until crystallization occurs). It is only with tetrahydrofuran as a solvent that no such broad-

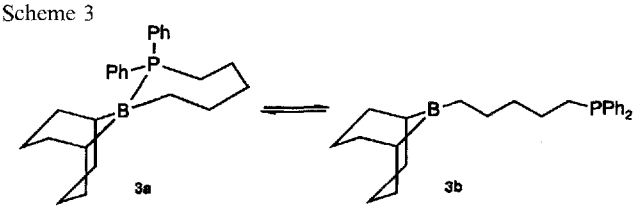
Figure 3. Chemical shift data [$\delta(^{31}P)$] of compound **3** in dichloromethane solution as a function of temperature [°C], with extrapolations to limiting shift values



ening or low-field shift of the signals is encountered: For this solvent the $\delta^{31}P$ parameters are largely independent of temperature.

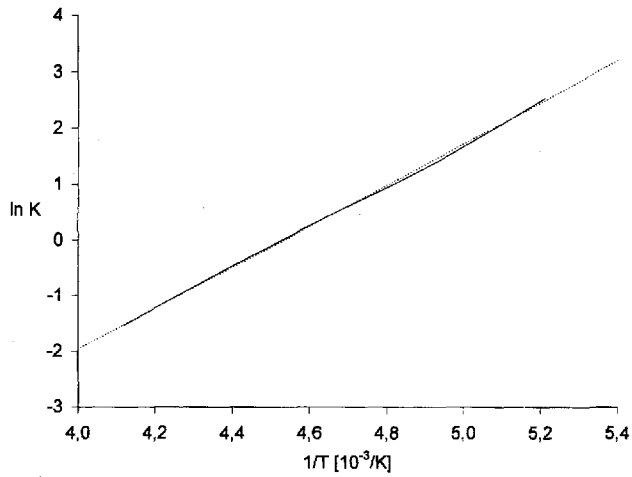
The experimental findings suggest that two compounds are present in equilibrium in solution: most likely the ring (**3a**) and the chain structure (**3b**), with **3a** as the low-temperature and **3b** as the high-temperature species. At temperatures where *both* species are present in significant amounts, there is obviously a facile interconversion which is rapid on the NMR time scale. Otherwise more than one signal would appear for a given temperature.

Scheme 3



For a two-component mixture, the equilibrium constant for the interconversion can be calculated from the chemical-shift data for each temperature. Figure 3 shows a plot of δ vs. T, with approximations for the low- and high-temperature limit shift values. Figure 4 presents a plot of $\ln K$ vs. $1/T$, with a satisfactory fit to a straight line for the numerical solution. Using the van't Hoff equation, ΔH of the reaction is calculated to be $-30.5(4)$ kJmol^{-1} (see the Experimental Section).

Figure 4. $\ln K$ as a function of $1/T$ [K] for the equilibrium constants relating **3a** and **3b** in dichloromethane solution



This enthalpy of the ring closing reaction can be taken as a measure of the P–B bond energy, which is found to be surprisingly small. It should be kept in mind, however, that the value may be strongly modified by differences in the solvent cages for the two forms (**3a**, **3b**), and that the entropy changes associated with the ring closure are not negligible.

The role of solvation is evident from the abnormal behaviour in tetrahydrofuran (above): With this strong donor solvent, no ring closure occurs down to the freezing temperature of the liquid. The enthalpy of ring closure is thus more than compensated by the thf addition to the borane end group of **3b** (**3c**).

In summary our results clearly demonstrate that phosphane–borane addition is a readily reversible process associated with only limited gains in potential energy. Although compounds **1**, **2** and **3a–c** are extreme cases in that the effects observed are strongly influenced by the steric constraints associated with the BBN cage, they nevertheless show very nicely the general trends in this class of compounds.

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Experimental Section

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves under nitrogen. – NMR: TMS as internal standard for ^1H and $^{13}C\{^1H\}$, H_3PO_4 (85% in H_2O) as external standard for $^{31}P\{^1H\}$ and $BF_3(Et_2O)$ as external standard for $^{11}B\{^1H\}$; Jeol-GX 400 and Jeol-GX 270. – MS: Finnigan MAT90. – 5-Bromo-1-pentene, $KPPh_2$, BH_3(thf) and 9-BBN were commercially available from Aldrich Inc.

4-Pentenyl(diphenyl)phosphane (**4**): 52 ml of a 0.5 M solution of $KPPh_2$ in tetrahydrofuran is added to 5-bromo-1-pentene (3.90 g, 26.2 mmol) in thf (50 ml) over a period of 1 h at −70°C. The reaction mixture is allowed to warm to room temperature and then refluxed for 1 h. The solvent is removed under reduced pressure and the phosphane is extracted from the residue with diethyl ether. After washing with water and drying over $MgSO_4$, the ethereal solution is distilled in a vacuum. Yield 5.05 g (76%), colourless liquid, b.p. 150°C/0.1 Torr. – ^1H NMR ($CDCl_3$, 20°C): δ = 1.64 (m, PCH_2CH_2), 2.13 (m, $PCH_2CH_2CH_2$), 2.25 (m, PCH_2), 5.06 (m, $CHCH_2$), 5.84 (m, $CHCH_2$), 7.37–7.49 (m, Ph). – $^{13}C\{^1H\}$ NMR (v.s.): δ = 25.1 [d, J(CP) = 17 Hz, PCH_2CH_2], 27.3 [d, J(CP) = 10 Hz, $PCH_2CH_2CH_2$], 35.0 [d, J(CP) = 13 Hz, PCH_2], 115.0 (s, $CHCH_2$), 128.3 [d, J(CP) = 7 Hz, C-*meta*], 128.3 (s, C-*para*), 132.5 [d, J(CP) = 19 Hz, C-*ortho*], 138.0 (s, $CHCH_2$), 138.8 [d, J(CP) = 13 Hz, C-*ipso*]. – $^{31}P\{^1H\}$ NMR (v.s.): δ = −15.9, s. – $C_{17}H_{19}P$ (254.31): calcd. C 80.29, H 7.53; found C 79.97, H 7.55. – MS (EI); *m/z*: 254 [M^+].

4-Pentenyl(diphenyl)phospane–Borane (**5**): A solution of 4-pentenyl(diphenyl)phosphane (**4**, 0.51 g, 2.0 mmol) in thf (10 ml) is treated with 2 ml of a 1 M solution of borane in thf. After 30 min at room temperature the solvent is removed from the reaction mixture in a vacuum. The residue is washed twice with pentane to remove unreacted phosphane. Yield 0.50 g (94%) colourless solid, m.p. 48°C. – ^1H NMR ($CDCl_3$, 20°C): δ = 0.6–1.6 (m, BH_3), 1.69 (m, PCH_2CH_2), 2.16–2.27 (m, $PCH_2CH_2CH_2$), 5.04 (m, $CHCH_2$), 5.77 (m, $CHCH_2$), 7.47–7.73 (m, Ph). – $^{13}C\{^1H\}$ NMR (v.s.): δ = 22.0 (s, $PCH_2CH_2CH_2$), 24.8 [d, J(CP) = 37 Hz, PCH_2], 34.6 [d, J(CP) = 15 Hz, PCH_2CH_2], 115.7 (s, $CHCH_2$), 128.6 [d, J(CP) = 7 Hz, C-*meta*], 129.4 [d, J(CP) = 55 Hz, C-*ipso*], 131.1 [d, J(CP) = 3 Hz, C-*para*], 131.9 [d, J(CP) = 9 Hz, C-*ortho*], 137.0 (s, $CHCH_2$). – $^{31}P\{^1H\}$ NMR (v.s.): δ = 16.3 br. s. – $^{11}B\{^1H\}$ NMR (v.s.): δ = −40.0 [d, J(BP) = 47 Hz]. – $C_{17}H_{22}BP$ (268.15).

[5'-(9-Borabicyclo[3.3.1]nonanyl)pentyl](diphenyl)phosphane (**3**): 9-BBN (0.69 g, 5.6 mmol) is added to a solution of 4-pentenyl(diphenyl)phosphane (**4**, 1.42 g, 5.6 mmol) in thf (10 ml). After refluxing for 1 h the solvent is removed under reduced pressure and the residue is washed with pentane. Yield 1.86 g (92%), colourless

oil. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 0.9–2.2 (m, aliphat.), 7.37–7.49 (m, Ph). – ^{13}C{^{1}H} NMR (v.s.): δ = 23.2 (s, 9-BBN-C$^\gamma$), 24.1 (s, CH_2CH_2B), 25.8 [d, J(CP) = 16 Hz, PCH_2CH_2], 27.8 (br. s, CH_2B), 28.0 [d, J(CP) = 10 Hz, $PCH_2CH_2CH_2$], 30.8 (br. s, 9-BBN-C$^\alpha$), 33.1 (s, 9-BBN-C$^\beta$), 34.3 [d, J(CP) = 13 Hz, PCH_2], 128.3 [d, J(CP) = 6 Hz, C-*meta*], 128.4 (s, C-*para*), 132.7 [d, J(CP) = 18 Hz, C-*ortho*], 138.9 [d, J(CP) = 12 Hz, C-*ipso*]. – ^{31}P{^{1}H} NMR (v.s.): δ = −15.0, s. – ^{11}B{^{1}H} NMR (v.s.): δ = 85.5 br. s. – $C_{25}H_{34}BP$ (376.34): calcd. C 79.79, H 9.11; found C 78.88, H 9.00. – MS (CI); *m/z*: 376 [M^+], 256 [$M^+ + 1 - B(C_8H_{14})$]. – VT – ^{31}P{^{1}H} NMR (CD_2Cl_2): δ (T, °C) = 3.3 (−91.3), 1.8 (−81.3), −0.5 (−71.2), −3.7 (−61.1), −7.5 (−50.6), −10.9 (−40.5), −13.4 (−30.6), −15.1 (−20.6), −16.3 (−10.6), −17.0 (−0.6); equations used for calculation:

$$K = \frac{x_c}{x_f} = \frac{1 - x_f}{x_f}, \quad \delta_{obs} = x_f \cdot \delta_f + x_c \cdot \delta_c, \quad x_f = \frac{\delta_{obs} - \delta_c}{\delta_f - \delta_c},$$

$$\frac{d \ln K}{d \frac{1}{T}} = -\frac{\Delta H_R}{R}$$

Structure Determination: A suitable crystal of compound **3** was mounted in a glass capillary and used for measurements of precise cell constants and collection of intensity data. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lp but not for absorption effects. The structure was solved by direct methods and refined against F^2. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atom with $U_{iso(fix)} = 1.5\ U_{eq}$ of the attached carbon atom.

Crystal Data: $C_{25}H_{34}BP$, M_r = 376.34, colourless crystals of dimensions 0.25 × 0.42 × 0.5 mm, triclinic, a = 9.194(1), b = 10.245(1), c = 12.867(2) Å, α = 67.68(1), β = 85.62(1), γ = 69.49(1)°, space group $P\bar{1}$, Z = 2, V = 1047.9(2) Å^3, D_{calcd} = 1.193 g cm^{-3}, F(000) = 408; Enraf Nonius CAD4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), T = −74°C. Data were corrected for Lorentz and polarization effects but not for absorption [μ(Mo-K_α) = 1.4 cm^{-1}]. From 4248 measured [$(\sin\theta/\lambda)_{max}$ = 0.62 Å^{-1}] and 4245 unique reflections, 4242 were used for refinement. The structure converged for 244 refined parameters to an $R(wR2)$ value of 0.0397 (0.1019). The function minimized was $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, $p = (F_o^2 + 2F_c^2)/3$; a = 0.0514, b = 0.54. Residual electron densities: +0.73/−0.35 eÅ^{-3}. Selected interatomic distances and angles are given in the figure caption. Further information on the X-ray structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-406403, the names of the authors, and the journal citation.

☆ Dedicated to Professor *Gottfried Huttner* on the occasion of his 65th birthday.

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