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1-Boryl-3,4-dimethylphosphole trimer: Synthesis, crystal structure and quantum chemical calculations

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Abstract

A novel cycloadduct of 1-boryl-3,4-dimethylphosphole was prepared by reaction of 3,4-dimethylphospholyl anion with monobromoborane–methylsulfide complex $(CH_3)_2S \cdot BH_2Br$ at −60 °C. It was characterized as a six-membered trimer by spectroscopic means, and its structure confirmed by an X-ray crystal analysis and quantum chemical calculations. Density functional theory calculations (B3LYP) showed that the cyclic trimer is by far more stable than the monomer, dimers or open-chain forms. Various molecular and spectroscopic properties of the borylphosphole monomer and trimer were evaluated. In particular, the changes of the ^{31}P NMR chemical shifts upon oligomerization were examined. The six-membered ring was demonstrated to exist preferentially in a chair-like conformation. Computed NMR chemical shifts (^1H, ^{13}C and a lesser extent ^{31}P) appear to be a highly sensitive analytical tool for distinguishing ring conformations having only small energy differences.
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1. Introduction

Boron–phosphorus compounds have not been as intensively studied as their boron–nitrogen counterparts [1]. Recently, the research in this field has nicely been developed with the discovery of novel boron–phosphorus derivatives with various degrees of B–P bonding [2].

The general tendency of simple units such as phosphinoboranes (R_2B-PR_2') is to associate through condensation with a donation of the lone pair of phosphorus into an empty 2p-orbital of boron. Monomeric phosphinoboranes, without steric or electronic shielding, readily associate to each other and thereby form four-, six- and eight-membered ring compounds with four-coordinated boron and phosphorus atoms [3]. The $[(CH_3)_2PBH_2]_n$ polymers have first been prepared by Burg and Wagner [4] using thermolysis of $(CH_3)_2PH \cdot BH_3$ at 150 °C for 40 h; this reaction gave a mixture of $[(CH_3)_2PBH_2]_n$ polymers, including mostly trimers, some tetramers and a trace of polymer. The hexa-phenyl-cyclo-triphosphino-borine $P_3Ph_6B_3H_6$ was also synthesized by Wagner and coworkers [5]. The synthesis was subsequently improved by Shaw and Smith [6]. More recently, Manners and coworkers [7–9] reinvestigated these reactions using a novel catalytic dehydrocoupling route for the synthesis of chain, cyclic and polymeric phosphinoboranes. This route has further been explored by Denis et al. [10] using $B(C_6F_5)_3$ as a new catalyst in the formation of P–B bonds. These macromolecules based on main group elements are of considerable current interest, especially owing to their great potential for accessing materials with fascinating and unexpected properties in significant applications [11–13].

(Ph$_2$P-BH$_2$)$_3$ (Me$_2$P-BH$_2$)$_3$
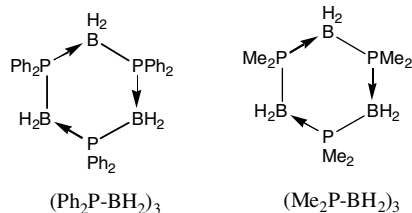
In this context, we have set out to explore a specific family of B–P compounds bearing four-coordinated boron and phosphorus atoms. In the work described here, we have attempted to prepare new cycloadducts in exploiting a peculiar behavior of the 3,4-dimethylphospholyl anion toward $(CH_3)_2S \cdot BH_2Br$. It turns out that the reaction ends up with an exclusive formation of a cyclic trimer. The novel compounds have been characterized with the aid of spectroscopic means, X-ray crystal analysis and ab initio quantum chemical computations.

2. Results and discussion

2.1. Synthesis and structure analysis of the product

The starting 3,4-dimethylphospholyl anion was prepared from 1-phenyl-3,4-dimethylphosphole [14] by cleavage reaction with lithium. This anion reacted with an excess of $CH_3)_2S \cdot BH_2Br$ at -60 °C. The process is summarized in Scheme 1. When the reaction was carried at low temperature, no monomeric phospholylborane $[(DMP)–BH_2]$ has been detected. The mass spectra of the final product clearly show the presence of a trimeric adduct $[(DMP)–BH_2]_3$ (m/z 372) as the highest molecular mass. The ^{31}P NMR spectrum points out a broad signal at 1.5 ppm, as observed in the case of other cyclic phosphorus-boron adducts. In the ^{1}H NMR spectrum, the BH_2 protons appear at 1.24 ppm and 1.54 ppm as broad massifs, the CH_3 of DMP at 2.06 ppm as a singlet and the olefinic protons at 6.38 ppm as a doublet with a very large $^2J(P–H)$ coupling of 33.64 Hz. The structure can unambiguously be confirmed by an X-ray analysis, whose skeleton is displayed in Fig. 1. The six-membered ring has a chair conformation as observed for the analogous trimers $[(CH_3)_2PBH_2]_3$ [15] and $[Ph_2PBH_2]_3$ [16]. A comparison of the mean bond lengths (Å) and angles (°) for these three compounds is collected in the Table 1.

The B–P distances vary in the range of 1.94–1.95 Å. The main difference concerns the CPC bond angle, which is intrinsically dependent on the cyclic nature.
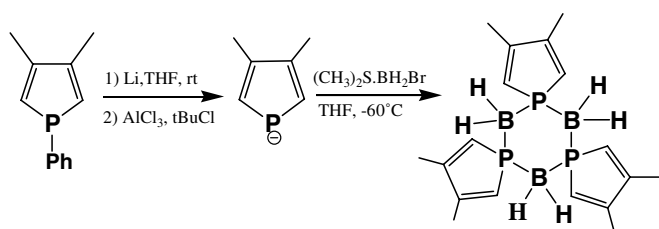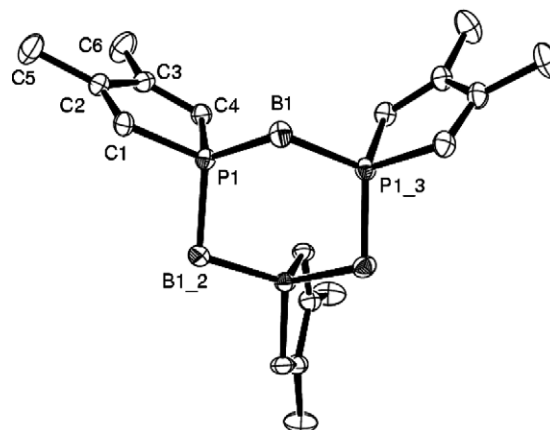

Fig. 1. Crystal structure of trimeric adduct. Significant bond distances (Å) and angles (degrees) P(1)–B(1) 1.946(2), P(1)–B(1_2) 1.953(2), P(1_3)–B(1) 1.953(2), P(1)–C(1) 1.791(2), P(1)–C(4) 1.792(2), C(1)–C(2) 1.347(2), C(2)–C(3) 1.479(2), C(3)–C(4) 1.345(2), B(1)–H(1A) 0.990, B(1)–H(1B) 0.990; C(1)–P(1)–C(4) 91.53(8), C(1)–P(1)–B(1) 111.11(8), C(4)–P(1)–B(1) 117.6(1), C(1)–P(1)–B(1_2) 111.79(8), C(4)–P(1)–B(1_2) 108.8(1), B(1)–P(1)–B(1_2) 114.0(1), H(1A)–B(1)–H(1B) 108.5, P(1)–B(1)–H(1A) 110.3, P(1)–B(1)–H(1B) 110.3.

Table 1
Comparison of mean bond lengths (Å) and angles (degrees) in B–P compounds

Parameter	[(Me$_2$C$_4$H$_4$P)-BH$_2$]$_3$[a]	[(Me$_2$C$_4$H$_4$P)-BH$_2$]$_3$[b]	[(Ph$_2$C$_4$H$_4$P)-BH$_2$]$_3$[c]
B–P	1.953 (2)	1.935 (9)	1.948 (2)
B–H	0.990	1.20 (8)	1.11 (2)
B–P–B	114.0 (1)	118 (1)	114.3 (1)
P–B–P	107.1 (1)	112.2 (9)	109.8–114.4
H–B–H	108.5	109	112 (2)
C–P–C	91.5 (8)	100.4 (9)	103.1 (1)

[a] This work.
[b] Ref. [15].
[c] Ref. [16].

2.2. Quantum chemical computations

Having established the identity of the six-membered trimer product, we now turn to a quantum chemical study of some aspects of its structure and properties. Although the phosphole monomers and their oligomers have recently been investigated [17–26], much attention has been paid to the linear polymeric structures. The longitudinal first hyperpolarizability of phosphinoborane oligomers $–(H_2P–BH_2)_n–$ and their dehydrogenated $–(PH–BH)_n–$ derivatives have also been determined using ab initio calculations [27]. In contrast, relatively little is known about 1-borylphospholes [18,23]. All calculations were carried out using the Gaussian 03 [28] and Turbomol [29] suites of programs.

2.2.1. Properties of borylphosphole

Let us first describe the main results on 1-boryl-substituted 1H-phospholes. In the parent BH_2-phosphole, the P-atom becomes markedly less pyramidal; the sum of the bond angles around P amounts to about 338°, as compared

Scheme 1.

with that of 293° in the un-substituted phosphole. Such a decrease of pyramidality obviously tends to induce a greater π-delocalization and the higher aromaticity of the phosphole ring. As a measure of such a change, the barrier to inversion at P in borylphosphole becomes thus negligible, being equal to about 1 kcal/mol. Optimised geometries and energies of both planar and pyramidal forms are given in Figure 1S, where S stands for Electronic Supplementary Information. The latter quantity is calculated to be 33, 17 and 4 kcal/mol in phosphine, phosphole, and phosphinoborane, respectively (using the same level of theory). This points out the strong effect of the boryl group on the P-inversion, and the appropriately substituted borylphospholes at the 2- and 5-positions are expected to have a practically planar tricoordinated P-atom.

As a consequence of the strong electron delocalization, the local charge distribution is also modified. This can be probed by means of the basicities. At the B3LYP/6-311++G(3df,2p) + ZPE level, the proton affinities (PA) of 1–BH_2-1H-phosphole are calculated to be 203, 210 and 201 kcal/mol at the P, C_α and C_β sites, respectively. In the parent phosphole molecule, the corresponding PA's are 202, 202 and 190 kcal/mol. Accordingly, the C_α-site clearly becomes the most favored protonation site following boryl substitution; the P-atom becomes less basic and the C_β-atom more basic. Thus, the proton affinity of the borylphosphole monomer is predicted as PA(1–BH_2-1H-phosphole) = 210 ± 2 kcal/mol. This corresponds to an increase of 8 kcal/mol relative to the unsubstituted parent compound.

It is worth noting that multi-configurational calculations using a complete active space method CASSCF (6,7), followed by the second order perturbation theory CASPT2 with the large ANO-L basis set, demonstrate that the two lowest excitations correspond to the frontier orbital transitions:

the first excitation: A^1A'' ($17a' \leftarrow 9a''$) $\leftarrow X^1A'$, $\Delta E =$ 3.5 eV, and $f = 0.03$;
the second excitation: B^1A' ($17a' \leftarrow 16a'$) $\leftarrow X^1A'$, $\Delta E = 3.9$ eV, and $f = 0.4$.

While the orbital $17a'$ corresponds to the LUMO, the orbitals $16a'$ and $9a''$ are the HOMO and HOMO-1, respectively. The following excitations occur at energy larger than 5 eV. Separate time-dependent density functional theory (TD-DFT) computations provided comparable results for excitation energies.

2.2.2. Dimers of borylphosphole

There are two distinct types of dimers of phosphinoboranes, namely, the open-chain and the four-membererd cycles. For the purpose of comparison, we have considered the dimers of phosphinoborane (BH_2–PH_2)$_2$ whose geometries and energies are given in Figure 2S (Electronic Supplementary Information). Although the dimerization is consistently exothermic, it is clear that the cyclic dimer is favored by 23 kcal/mol over its open-chain isomer. Fig. 2 displays the geometries of the cyclic and chain-like dimers of borylphosphole. Again the four-membered ring **DIM-a** is substantially more stable (by 26 kcal/mol) than the open-chain**DIM-b**. In both cases, the dimerization energy amounts to about −30 kcal/mol. The B–P distances in the cyclic forms are found to be around 2.0 Å, slightly shorter in the open-chain forms.

2.2.3. Trimers of borylphosphole

Using a similar procedure, both cyclic and open-chain forms of the trimers of phosphinoborane and borylphosphole were located. While the former are given in Figure 3S, the latter are displayed in Fig. 3. Due to the larger size of the molecules considered, only the 6-31G(d,p) basis set was used for borylphosphole trimers in conjunction with the DFT/B3LYP method.

The six-membered rings of (H_2P–BH_2)$_3$ are by far more stable than the open-chain counterparts (Figure 3S). The chair form **TRIM-3** turns out to be the lowest-energy isomer having a trimerisation energy of −72 kcal/mol relative to three separated monomers. This is about three times as large as that of the chain-like **TRIM-4** and **TRIM-5** counterparts. The species bearing a bridge B–H–B bond, **TRIM-2**
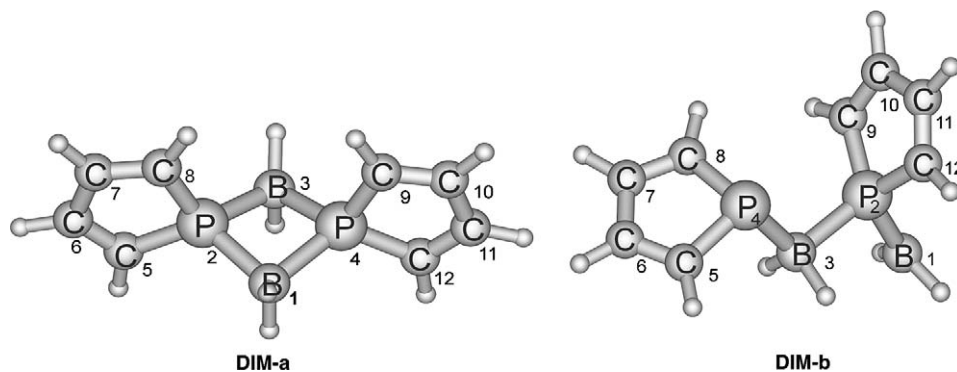

DIM-a   DIM-b

Fig. 2. Selected bond lengths (A) and bond angle (degrees) of the two dimers of borylphosphole obtained using B3LYP/6-311++G(d,p): **DIM-a:** B_1P_2 2.006, P_2B_3 2.006, B_3P_4 2.006, P_4B_1 2.006, P_2C_5 1.804, C_5C_6 1.356, C_6C_7 1.468, C_7C_8 1.358, C_8P_2 1.808, P_4C_9 1.356, C_9C_{10} 1.356, $C_{10}C_{11}$ 1.468, $C_{11}C_{12}$ 1.356, P_4C_{13} 1.808, $\angle P_4B_1P_2$ 87.5, $\angle B_1P_4B_3$ 89.2, Dih($B_1P_2B_3P_4$) −19.5, Dih($C_{12}P_4P_2C_9$) 0.0 **DIM-b**: B_1P_2 1.903, P_2B_3 2.008, B_3P_4 1.995, P_4C_5 1.805, C_5C_6 1.366, C_6C_7 1.452, C_7C_8 1.366, C_8P_4 1.807, P_2C_9 1.806, C_9C_{10} 1.355, $C_{10}C_{11}$ 1.470, $C_{11}C_{12}$ 1.354, $C_{12}P_2$ 1.806, $\angle B_1P_2B_3$ 97.1, $\angle P_2B_3P_4$ 108.9, Dih($B_1P_2B_3P_4$) −178.7.
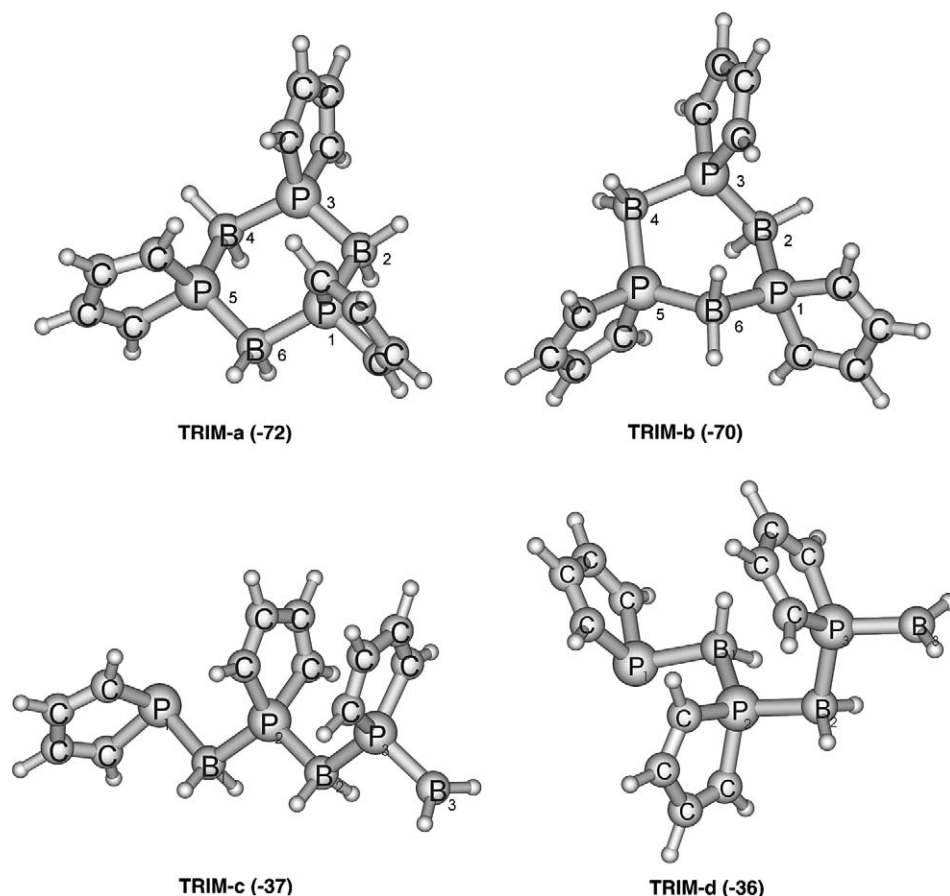
Fig. 3. Selected bond lengths (Å) and bond angle (degrees) of some cyclic and open trimers of borylphosphole obtained using B3LYP/6-31G(d). Values in parentheses are energies in kcal/mol relative to three separated monomers. **TRIM-a**: P_1B_2 1.974, B_2P_3 1.974, P_3B_4 1.974, B_4P_5 1.974, P_5B_6 1.974, B_6P_1 1.974, P_1C 1.817, CC 1.354, CC 1.469, $\angle P_1B_2P_3$ 109.2, $\angle B_2P_3B_4$ 116.1, $\angle P_3B_4P_5$ 109.2, $\angle B_4P_5B_6$ 116.0, Dih($P_1B_2P_3B_4$) −51.3, Dih($B_2P_3B_4P_5$) 51.3, Dih($P_3B_4P_5B_6$) −51.3. **TRIM-b**: P_1B_2 1.980, B_2P_3 1.974, P_3B_4 1.983, B_4P_5 1.983, P_5B_6 1.974, $B_6P_1$1.980, $\angle P_1B_2P_3$ 108.19, $\angle B_2P_3B_4$ 114.80, $\angle P_3B_4P_5$ 108.28, $\angle B_4P_5B_6$ 114.79, $\angle P_5B_6P_1$ 108.20, Dih($P_1B_2P_3B_4$) −63.32, Dih($B_2P_3B_4P_5$) 31.68, Dih ($P_3B_4P_5B_6$) 32.00, Dih($B_4P_5B_6P_1$) − 63.37. **TRIM-d**: P_1B_1 2.030, B_1P_2 2.057, P_2B_2 1.996, P_2B_3 2.086, B_3P_3 1.943, $\angle P_1B_1P_2$ 108.7, $\angle B_1P_2B_2$ 116.4, $\angle P_2B_2P_3$ 109.5, $\angle B_2P_3B_3$ 104.5, Dih($P_1B_1P_2B_2$) 105.5, Dih($P_2B_2P_3B_3$) −169.6, Dih($B_1P_2B_2P_3$) 66.3.

(−49 kcal/mol), becomes more stable then the open-chain isomer, but it remains less stable the cyclic chair form.

A similar feature emerges for the trimeric forms of borylphosphole. As seen in Fig. 3, the chair six-membered ring **TRIM-a** is found to be the lowest-energy trimer. The boat form **TRIM-b** is about 1 kcal/mol less stable. The corresponding trimerization energy of about −72 kcal/mol is twice as large as that of the open-chain isomers **TRIM-c** and **TRIM-d**. Relative to the simpler phosphinoborane, the phosphole moieties do apparently not induce an additional stabilization of the oligomers. In going from the dimer **DIM-a** to the trimer **TRIM-a**, the energy gain by cyclic product is almost triple, likely arising from the formation of two additional B–P bonds. The calculated B–P bond distances of 1.97 Å (Fig. 3) are close to the crystal structure results of 1.95 Å (Fig. 1 and Table 1). The difference of 0.02 Å could be accounted for by the smaller basis set employed for this system. The B–P distances in the open-chains are consistently larger (about 2.0 Å). Overall, geometrical aspects derived from ab initio calculations lend a further support for experimental results on the formation of the six-membered trimer of borylphosphole.

2.2.4. Some properties of the six-membered trimer

In an attempt to gain further insights into the structure of the cyclic product, we have calculated some of its electronic and spectral properties.

2.2.4.1. Frontier orbitals. Fig. 4 illustrates the HOMO and LUMO of the model six-membered chair ring. It is remarkable that the HOMO is of σ-character centered on the opposite B–P bonds whereas the LUMO corresponds to a P lone pair. It is thus expected that ionization tends to shorten these B–P bonds but electron attachment does not induce large modifications of the molecular skeleton.

2.2.4.2. Chemical shifts. One of the typical spectral properties characterizing the P-containing compounds is the ^{31}P NMR chemical shift as they are very sensitive to the struc-
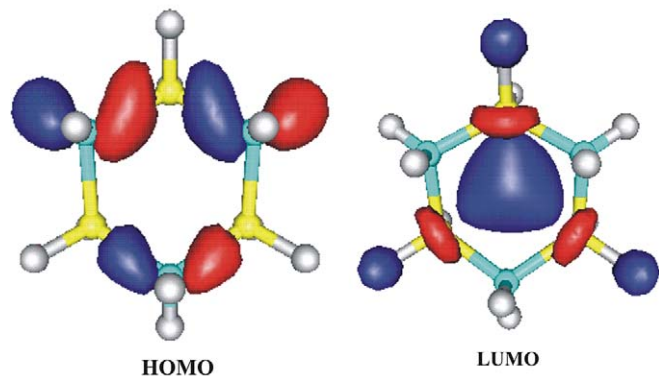
Fig. 4. Shape of the frontier orbitals (HOMO: a″ and LUMO: a′) of the six-membered ring of $(H_2P–BH_2)_3$ at B3LYP/6-311++G(d,p).

tural modifications. In order to have a direct comparison with the available experimental data reported in Section 3, the 1-boryl-3,4-dimethylphosphole trimer has also been considered. We refer to this Section for the experimental values quoted hereafter. Table 2 lists the relevant calculated values in three distinct trimers in their most stable chair form. It is confirmed that the five-membered phosphole ring markedly affects the $\delta(^{31}P)$ by a shift of 109 ppm in going from phosphinoborane to borylphosphole trimer. Attachment of two methyl groups at both positions 3 and 4 of the latter induces a smaller shift of 11 ppm. For the largest trimer, the calculated value (3 ppm) is in agreement with the measured one (1.5 ppm). It is rather difficult to evaluate accurately the ^{31}P NMR properties using DFT methods due to the inherent self-interaction errors [30,31].

There is practically no significant and detectable difference (0.4–0.6 ppm) between the chemical shifts of the three P atoms within one chair-like ring. On the contrary, it seems possible to distinguish the chair-like form from the boat-like one. In the latter, the chemical shift of P_1-atom is significantly split from those of P_2 and P_3 that remains equivalent. As a matter of fact, in the dimethyl derivative, the boat-like cycle exhibits the values $\delta(^{31}P)$ of −6.4 ppm for P_1 and −2.9 ppm for both P_2 and P_3. Thus a conformational change induces a shift of 9 ppm on P_1 and also a splitting of the relevant peak.

It is however possible to evaluate, with higher accuracy, the chemical shifts of carbon and hydrogen nuclei using DFT calculations. The calculated results using GIAO

method with B3LYP in conjunction with 6–31G(d,p) basis set for both ^{13}C and ^1H chemical shifts of all atoms in the two chair-like cyclic trimers examined are recorded in Tables 1S and 2S (Electronic Supplementary Information). It is remarkable that for ^{13}C chemical shifts, there is mostly one set of values in the 1-borylphosphole trimer, namely around 132–133 ppm for both C_α and C_β atoms. Incorporation of two methyl groups at both C_β positions 3 and 4 induces a significant splitting into two distinct sets of values centered at 128 for C_α atoms, and 145–146 ppm for C_β atoms. The methyl carbons are characterized by chemical shifts of around 19 ppm. These calculated values (cf. Table 1S) compare quite favorably with the $\delta(^{13}C)$ values observed at 128, 152 and 18 ppm.

It is also remarkable that the ^1H chemical shifts (Table 2S) are even more sensitive with respect to methylation of the phosphole rings. Methyl substitution does not only allow to differentiate between both H(B) and H(C) nuclei, but also reduce substantially the absolute shifts. Overall, the three sets of calculated $\delta(^1H)$ values of 1.0–2.0, 6.3–6.5 and 2.0 ppm agree well with the experimental results of 1.24–1.54 ppm for H(B), 6.38 ppm for H(C), and 2.06 ppm for H of methyl.

In summary, calculations of the chemical shifts for three available C, H and P nuclei lend further supports not only for the formation of the six-membered trimer, but also for its preferred existence in a chair-like conformation.

2.2.4.3. Vibrational modes. We wish to gain some additional pieces of information in analyzing the vibrational modes. However, due to the large number of normal modes present in the phosphole trimers, the resulting spectra are quite rich and complex, and such an analysis is becoming rapidly tedious. Therefore, we have carried out a vibrational analysis only on the model phosphinoborane trimer $(BH_2–PH_2)_3$ whose simulated IR spectrum is shown in Figure 4S. The calculated vibrational frequencies and their assignments are summarized in Table 4S. The forms of normal modes are described by the percentage potential energy distribution (% PED). Together, the calculated results suggest that the B–H stretch modes could correspond to characteristic IR peaks centered with high intensity at the region of 2600–2550 cm^{-1}.

It is of interest to examine the normal modes associated with the motions of the six-membered ring. The corresponding modes are vividly illustrated in Fig. 5. As

Table 2
The ^{31}P chemical shifts (δ, in ppm) of trimer compounds of phosphinoborane $(H_2P–BH_2)_3$, 1-boryl 1*H*-phosphole $(C_4H_4P–BH_2)_3$ and 1-boryl-3,4-dimethylphosphole (DMP–BH$_2$) using the GIAO method at the B3LYP/6-31G(d,p) level[a]

Atoms	$(H_2P–BH_2)_3$		$(C_4H_4P–BH_2)_3$		$(Me_2C_4H_4P—BH_2)_3$		
	σ	δ	σ	δ	σ	δ	Expl.
P1	475.6	−123.6	337.9	14.1	348.8	3.3	1.5
P2	475.5	−123.4	338.4	13.7	349.4	2.7	
P3	475.5	−123.4	337.9	14.1	349.2	2.9	

[a] Isotropic magnetic shielding is given as σ. All δ values are referenced to the σ [B3LYP/6-31G(d,p)] of PH$_3$ value of 592.1 ppm.
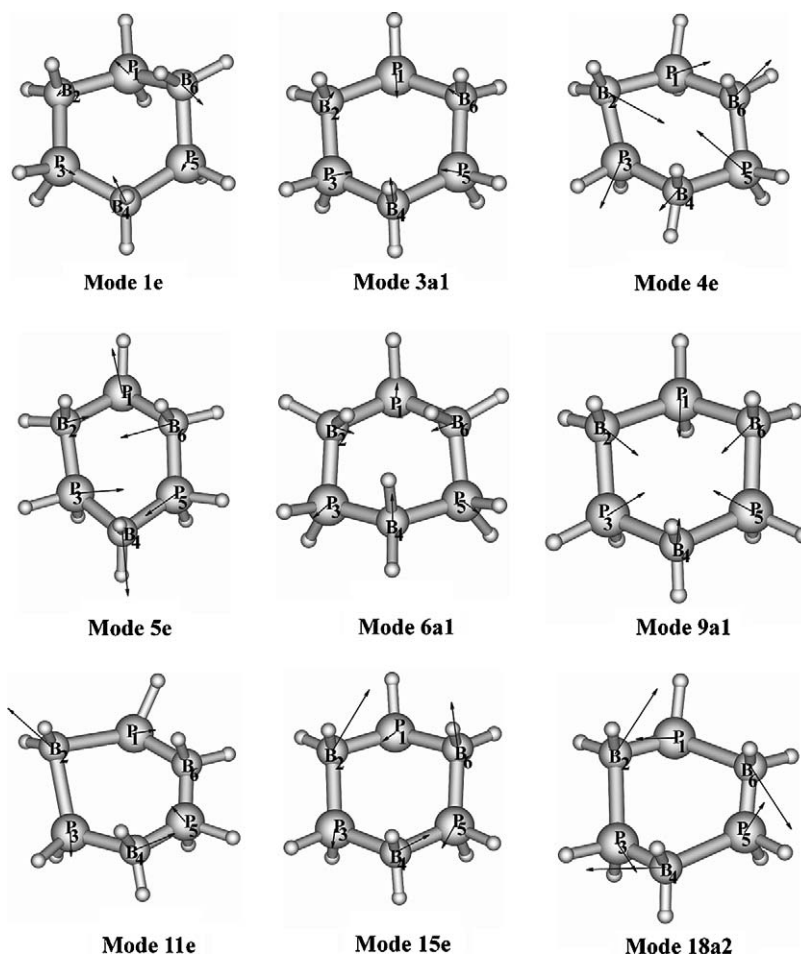
Fig. 5. Illustration of the normal modes associated with the ring motions in $(H_2P–BH_2)_3$.

expected, all the normal modes displayed involve the motions of all heavy atoms.

In summary, we have combined experimental synthesis, crystal structure analysis and ab initio calculations to study an oligomer of borylphosphole, which has been prepared and identified for the first time. All the approaches employed, either experimental or theoretical, concur with each other confirming the formation of a cyclic trimer. In addition, the six-membered ring has been demonstrated to exist in a preferred chair-like conformation. The computed NMR chemical shifts (^{1}H, ^{13}C and a lesser extent ^{31}P) appear to be a highly sensitive analytical tool for distinguishing conformations having small energy differences.

3. Experimental section

All reactions were performed under nitrogen; the solvents were purified, dried and degassed by standard techniques. NMR spectra were recorded on a multinuclear Bruker AC 200 SY spectrometer operating at 300.13 for ^{1}H, 75.47 for ^{13}C and 121.50 MHz for [31]P. Chemical shifts are expressed in parts per million (ppm) downfield from internal tetramethylsilane (^{1}H and ^{13}C) and external 85%

aqueous H_3PO_4(^{31}P). Mass spectra (EI) were obtained at 70 eV by the direct inlet method.

3.1. Synthesis of trimeric adduct of 1-boryl-3,4-dimethylphosphole

At $-60\,^{\circ}C$, an excess of $(CH_3)_2S \cdot BH_2Br$ (1.5 mL) is added to a solution of phospholyl anion prepared from 4 g of 1-phenyl-3,4-dimethylphosphole (20 mmol) and Li, in 50 mL of THF. The reaction is stirred magnetically while the temperature is elevated to room temperature. The ^{31}P NMR spectrum of the reaction mixture shows the presence of several peaks from -3 to $+3$ ppm.

The solution is then evaporated and chromatographed on SiO_2 with the eluent hexan/CH_2Cl_2: 2/1. We isolated 0.6 g of 1–Boryl-3, 4-Dimethylphosphole trimer as white crystals (25% yield).mp 56–60 $^{\circ}C$.

Slowly recrystallisation in CH_2Cl_2/hexane gives single crystals for X-ray.

NMR [31]P (CH_2Cl_2), $\delta = 1.5$ (broad). [1]H ($CDCl_3$), $\delta = 1.24$ and 1.54 (s, 2H, BH_2); 2.06 (s, 6H, CH_3); 6.38(d, $^2J(P–H) = 33.64$ Hz, 2H, olefinic H). [13]C ($CDCl_3$), $\delta = 18.18$ (d, $^4J(P–H) = 9$ Hz, CH_3); 128.01 (dd, $^1J(C–P) = 61.1$ Hz, $= CH$); 151.98 (s, $=$ C).

MS: *m/z* 372 ($M^+ +1$, 12%); 247 (M^+, Dimer, 14%), 123 ($M^+ -1$, Monomer, 100%).

Elemental analysis (Found: C, 58.47; H, 8.35. Calc. for $C_{18}H_{30}B_3P_3$: C, 58.15; H, 8.13%).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.06.011.

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