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A new *nido*-5-vertex cluster, phosphacarba-*nido*-pentaborane, 2-^{t}Bu-1,2-PCB$_3$H$_5$†

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The gas-phase reaction of the phosphaalkyne P≡C^{t}Bu with tetraborane(10), B$_4$H$_{10}$, yields the *nido* five-vertex phosphacarbaborane cluster compound 2-^{t}Bu-1,2-PCB$_3$H$_5$ 2 with an unusual ^{31}P NMR peak shift of −500.5 ppm.

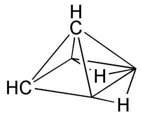
Syntheses of main-group heteroboranes[1] have been dominated by carbaboranes[2] for decades but recently there has been intense research on heteroboranes with phosphorus,[3] nitrogen[4] and silicon[5] cluster atoms. A naked P vertex is isolobal with a CH vertex so phosphaboranes and phosphacarbaboranes are structural analogues of the corresponding carbaboranes. A classic route into carbaborane chemistry involves the insertion of the two unsaturated carbon atoms of an alkyne into a boron cluster. For example tetraborane, B$_4$H$_{10}$, reacts with ethyne to yield 1,2-C$_2$B$_3$H$_7$,[6] the only heteroborane with a *nido*-5-vertex geometry reported prior to the work reported here.[7]

$$\mathrm{B_4H_{10} + HC{\equiv}CH \rightarrow 1{,}2\text{-}C_2B_3H_7}\ \mathbf{1} \qquad (1)$$

Phosphaalkynes, such as P≡C^{t}Bu, show similar chemical behaviour to alkynes in a wide variety of their reactions.[8] Here we report the reaction of P≡C^{t}Bu with B$_4$H$_{10}$ to form the novel phosphacarbaborane 2-^{t}Bu-1,2-PCB$_3$H$_5$ **2**, the second known heteroborane with a *nido*-5-vertex geometry.

$$\mathrm{B_4H_{10} + P{\equiv}C^tBu \rightarrow 2\text{-}^tBu\text{-}1{,}2\text{-}PCB_3H_5}\ \mathbf{2} \qquad (2)$$

In a typical experiment, a mixture of B$_4$H$_{10}$ (0.37 mmol) and P≡C^{t}Bu (0.37 mmol) was expanded into a 1 L bulb held at 70 °C, and the gaseous reaction mixture monitored continuously by mass spectrometric techniques described earlier.[9] After *ca*. 18 min, when all the phosphaalkyne (*m*/*z* 100) had reacted, the contents of the bulb were condensed into a U-trap at −196 °C. The contents of the trap were then warmed slowly, and separated on a cold column. The fractions were monitored by mass spectrometry, and the fraction leaving the column over the temperature range −57 to −35 °C with a cut-off at *m*/*z* 138 consisted of a pure sample of 2-^{t}Bu-1,2-PCB$_3$H$_5$ **2** (0.06 mmol, 15%).



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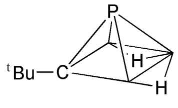

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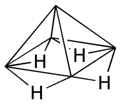

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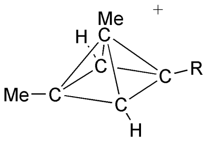

4 R = H
5 R = Me

Compound **2** decomposes on exposure to air and at room temperature in the liquid phase but is stable in the gas phase and in solution. The accurate ion mass spectrum of **2** is consistent with a formulation of PB$_3$C$_5$H$_{14}$ (observed 138.1103, calculated for PB$_3$C$_5$H$_{14}$ 138.1112). The ^{1}H NMR spectrum of **2** has a single peak corresponding to the *tert*-butyl group. The boron-decoupled ^{1}H spectrum showed three additional peaks assigned to hydrogens attached to boron. Line-narrowed boron NMR spectra for **2** are shown in Fig. 1; the proton-decoupled ^{11}B spectrum comprises two doublets of intensity ratio 2 : 1. The splittings are attributed to coupling to phosphorus, and their magnitudes indicate that all borons are directly bonded to the phosphorus atom. The only *nido*-geometry that fits these NMR observations is 2-^{t}Bu-1,2-PCB$_3$H$_5$. The un-decoupled ^{11}B spectrum (Fig. 1) shows the peak patterns expected from couplings of the boron atoms with the phosphorus atom and their *exo*- and bridging hydrogens.

Of the NMR data obtained for **2**, the most interesting observation is the very high field ^{31}P NMR shift, −501 ppm. White phosphorus P$_4$ is usually taken to be the high field limit in ^{31}P NMR spectroscopy (−488 ppm in CS$_2$ solution).[10] As far as we are aware the shift observed for **2** is the most negative value found in solution-state ^{31}P NMR spectroscopy. Shifts corresponding to the apical atom in the related *nido*-compounds **1** (δ_C −21.5 ppm), the borane B$_5$H$_9$ **3** (δ_B −52.6 ppm), the carbocations Me$_2$C$_5$H$_3^+$ **4** (δ_C −23.0 ppm)[11] and Me$_3$C$_5$H$_2^+$ **5** (δ_C −20.9 ppm)[12] are typically to high field. The high value observed for 2-^{t}Bu-1,2-PCB$_3$H$_5$ is therefore not unexpected.

Excellent agreements have been demonstrated between experimental and theoretical geometries for 1,2-C$_2$B$_3$H$_7$ and

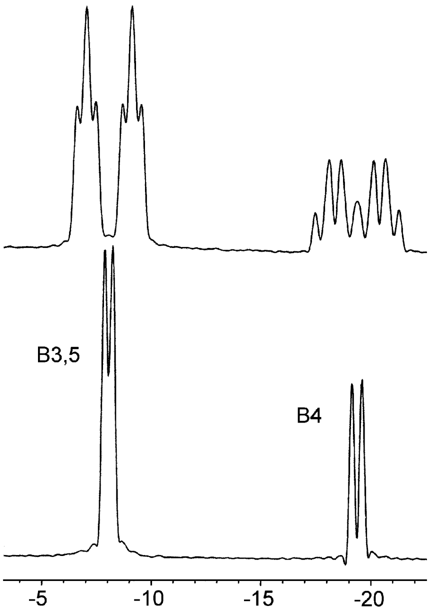

Fig. 1 Line-narrowed ^{11}B and ^{11}B{^{1}H} NMR spectra of 2-^{t}Bu-1,2-PCB$_3$H$_5$ **2**, ^{11}B NMR data for **2**: −8.1 (ddd, J_{BH_t} 167, J_{BH_μ} *ca*. 44, J_{BP} 24 Hz), −19.4 (dtd, J_{BH_t} 162, J_{BH_μ} *ca*. 48, J_{BP} 35 Hz).

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† Electronic supplementary information (ESI) available: rotatable 3-D molecular structure diagrams of MP2-optimised geometries for 2-^{t}Bu-1,2-PCB$_3$H$_5$ **2**, 1-^{t}Bu-2,1-PCB$_3$H$_5$ and P$_4$ in CHIME format. See http://www.rsc.org/suppdata/cc/b2/b204409a/

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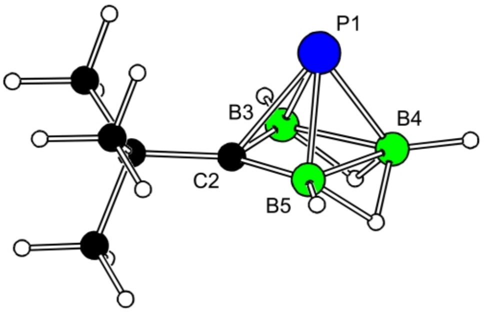

Fig. 2 MP2/6-31G* optimised geometry of 2-^{t}Bu-1,2-PCB_3H_5 **2**. Selected bond lengths (Å), P1–C2 2.04, P1–B3/5 1.99, P1–B4 1.93, C2–B3 1.54, B3–B4 1.87.

B_5H_9.[9,13,14] Fig. 2 shows the MP2/6-31G* (Gaussian98[15]) optimised geometry of 2-^{t}Bu-1,2-PCB_3H_5 with the expected square pyramidal *nido*-cluster; selected bond lengths are given. The structural dimensions and bond angles associated with the open face are virtually identical to those obtained for 1,2-$C_2B_3H_7$, both computationally (optimisations at the MP2/6-31G* level of theory) and from gas-phase electron diffraction studies.[9] The alternative isomer, 1-^{t}Bu-2,1-PCB_3H_5, is computed to be only *ca* 2.3 kcal mol^{-1} higher in energy compared to **2**. It is therefore possible that this species is formed in the reaction reported here, but is not isolated experimentally.

Calculated shifts for MP2- (or DFT-) optimised geometries of the four known *nido*-5-vertex compounds (**1**, **3–5**)[16] and larger phosphacarbaboranes[3,17] have so far resulted in good agreement with their observed NMR shifts. Comparison between experimental and theoretical[15] (GIAO-B3LYP/6-311G*//MP2/6-31G*) ^{11}B, ^1H and ^{31}P NMR chemical shifts listed in Table 1 for 2-^{t}Bu-1,2-PCB_3H_5 **2** show excellent agreement. At the same levels of theory, P_4 has a calculated peak shift of −539 ppm, which differs from the calculated ^{31}P shift for **2** by only 17 ppm.

Table 1 Observed and calculated ^{11}B, ^1H and ^{31}P NMR chemical shifts for 2-^{t}Bu-1,2-PCB_3H_5

	Observed	Calculated
^{11}B		
B3,5	−8.1	−11.6
B4	−19.4	−22.0
^1H		
B(3,5)H	2.89	3.03
B(4)H	2.28	2.72
Me	1.00	1.11
μ-H	−2.88	−2.83
^{31}P		
P1	−501	−522

The phosphaalkyne reaction described here is the only known direct route to a phosphacarbaborane from a borane cluster. The reaction of PCl_3 with a *nido*- or *arachno*-carbaborane cluster usually generates a phosphacarbaborane with a naked vertex whereas, with $RPCl_2$, a phosphacarbaborane with an RP vertex is produced.[3,18] As reactions of boranes and carbaboranes with alkynes often produce carbaboranes,[2] the parallel reactions of these boranes and carbaboranes with P≡C^{t}Bu may yield other new phosphacarbaboranes. Interestingly, however, the reactions between the borane adducts $B_{10}H_{12}L_2$ (L = SMe_2, NCMe) and P≡C^{t}Bu do not yield phosphacarbaboranes.[19]

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