One-pot transformation of cyclic phosphine oxides to phosphine–boranes by dimethyl sulfide–borane

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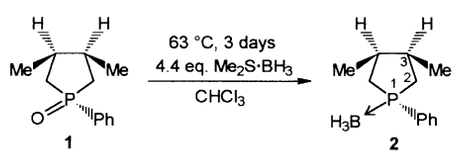
Different types of cyclic phosphine oxides, such as tetrahydrophosphole oxide **1**, phosphabicyclo[3.1.0]hexane 3-oxide **8** and phosphabicyclo[2.2.1]heptene 7-oxides **10** and **12** were efficiently converted to phosphine–boranes **2**, **9**, **11** and **13**, respectively, under relatively mild conditions by reaction with 4.4 equivalents of dimethyl sulfide–borane. The more strained hetero-ring the starting phosphine oxide (in general **16**) has, the easier to accomplish the change in the P-function, that takes place through the corresponding phosphine intermediate (**20**). It is noteworthy that the imide carbonyl groups in starting materials **10** and **12** were fully reduced by the borane to give **11** and **13** respectively.

Introduction

A survey of the recent literature confirms that the P-heterocyclic derivatives of phosphine–boranes are of interest.[1–7] Phosphine–boranes can be regarded as protected phosphines and hence they are precursors of phosphines.[8,9] On the other hand, the complexation at the phosphorus atom may affect the reactivity of the other functions in the molecule.[10] The most general way to synthesize phosphine–boranes involves the reaction of phosphines, obtained from the phosphine oxides by deoxygenation, with dimethyl sulfide–borane (BMS) or with tetrahydrofuran–borane.[8] The possibilities for the application of ring enlargements in the preparation of cyclic phosphine–boranes have also been explored.[4] It was most interesting to find that the bridging P=O moiety of the phosphole oxide dimers could easily be converted to a phosphine–borane unit by reaction with three equivalents of the BMS reagent.[11] Noteworthy is that the transformation was selective; the electron-poor double bond of the starting material remained intact. In other instances, the BMS reagent could, however, be well utilised in the selective reduction of the double bond of cyclic and acyclic vinylphosphine oxides.[12,13]

The purpose of this paper is to discuss the scope and limitations of the application of dimethyl sulfide–borane in the synthesis of cyclic phosphine–boranes from the *P*-oxides.



Scheme 1

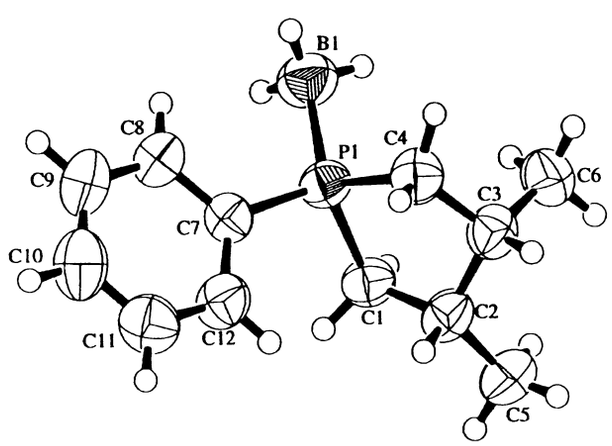


Fig. 1 Perspective view of **2**; hydrogen atoms are shown, but not labeled.

Results and discussion

Testing the simplest model, we found that the reaction of dimethyl(phenyl)tetrahydrophosphole oxide **1** with a considerable excess (4.4 equivalents) of the BMS reagent afforded phosphine–borane **2** after three days' heating at the boiling point of chloroform (Scheme 1). The prolonged reaction time was crucial from the point of view of the quantitative conversion. Column chromatography furnished product **2** (in 86% yield) which was characterised by ^{31}P, ^{11}B, ^{13}C and ^{1}H NMR, as well as mass spectroscopic methods. The ^{13}C and ^{1}H NMR spectra were consistent with the symmetry of compound **2**. The relative P-configuration in **2** was assigned on the basis of single crystal X-ray analysis (Fig. 1). The same stereochemistry was assumed to exist in starting dihydrophosphole oxide **1**. The selected bond parameters for phosphine–borane **2** are listed in Table 1. The steric crowding due to the two methyl groups on the same side of the five membered ring distorts the ring to a twisted conformation, hence the C_1–C_2–C_3–C_4 torsion becomes *gauche* with C_5-Me in a pseudo-equatorial position and with C_6–Me occupying a pseudo-axial position. The C_1–P_1–C_4–C_3 and C_4–P_1–C_1–C_2 torsion angles are of 17.8 and 8.8°, respectively (Table 1). The phosphorus atom lies at a distance of

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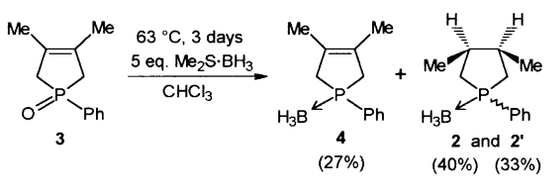
Table 1 Selected bond lengths (Å) angles (°) and torsion angles (°) for **2**

P(1)–C(7)	1.796(4)
P(1)–C(1)	1.810(4)
P(1)–C(4)	1.838(4)
P(1)–B(1)	1.886(5)
C(7)–P(1)–C(1)	108.3(2)
C(7)–P(1)–C(4)	107.2(2)
C(1)–P(1)–C(4)	95.5(2)
C(7)–P(1)–B(1)	113.7(2)
C(1)–P(1)–B(1)	115.6(2)
C(4)–P(1)–B(1)	114.9(3)
B(1)–P(1)–C(7)–C(8)	−13.9(4)
C(1)–P(1)–C(4)–C(3)	17.8(3)
C(4)–P(1)–C(1)–C(2)	8.8(3)
C(1)–C(2)–C(3)–C(4)	47.5(4)

0.030 Å from the plane defined by the C_1, C_2, C_3 and C_4 atoms (rms deviation of 0.191 Å). Despite their different size, the two substituents of the phosphorus atom are of similar distance from the ring plane (1.524 and 1.533 Å for P–C_7 and P–B, respectively).

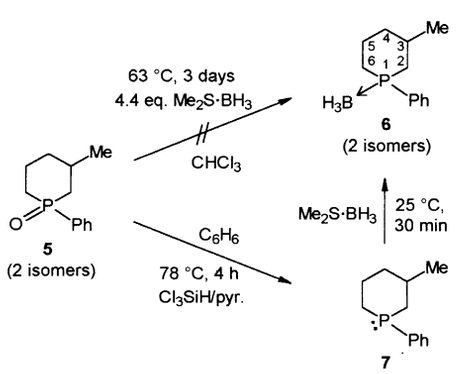
A similar reaction of 2,5-dihydrophosphole oxide **3** with dimethyl sulfide–borane led to a mixture of the borane derivative of the dihydrophosphole (**4**) and that of the tetrahydrophosphole consisting of isomers **2** and **2′** as suggested by the ^{31}P NMR spectrum and the FAB-MS measurement (Scheme 2).



Scheme 2

Traces of tetrahydrophosphole oxide **1** could also be detected. Compounds **1** and **4** are possible intermediates for the isomers (**2** and **2′**) of the tetrahydrophosphole–borane. The **4** ⟶ **2** + **2′** transformation may take place through hydroboration. No efforts were made to separate the components of the crude reaction mixture.

Applying similar reaction conditions, we were not able to convert phosphinane oxide **5** to borane **6**; even after three days' reflux in chloroform, oxide **5** was recovered unchanged (Scheme 3). Phosphine–borane **6** could, however, be prepared through phosphine **7**. The phosphine (**7**) was obtained by a conventional deoxygenation of the oxide (**5**) using trichlorosilane,[14] to give after reaction with borane the desired product (**6**) characterised by ^{31}P, ^{11}B and ^{13}C NMR, as well as FAB-MS (Scheme 3).



Scheme 3

It seemed to be interesting to examine whether phosphabicyclo[3.1.0]hexane 3-oxide **8** behaves as a cyclic phosphine oxide of a five- or a six-membered ring in reaction with borane. We learnt that phosphine oxide **8** was efficiently (in 81% yield) transformed to borane **9** under the conditions applied above (Scheme 4). The spectral parameters of product **9** were identical with those of an authentic sample.[4] The relative configuration in **9** was confirmed by single crystal X-ray analysis (Fig. 2) suggesting that the sterochemistry of the phosphorus atom in starting material **8** was preserved.[15] Selected bond parameters for product **9** can be found in Table 2. Similarly to phosphine–borane **2**, compound **9** also exhibits a significantly shorter exocyclic P–C bond as compared to the endocyclic ones. The five-membered hetero-ring of **9** has an envelope conformation with the phosphorus atom on the flap; its distance from the C_2–C_1–C_4–C_3 plane is 0.541 Å (Table 2). The phenyl group is placed in a pseudo-equatorial position, while the borane unit occupies the pseudo-axial position. The angle between the planes of the phenyl ring and the five-membered ring (110.4°) is different from that found in **2** (101.1°), bringing about the steric proximity of C_3 and the edge of the phenyl ring in **9**.

Table 2 Selected bond lengths (Å) angles (°) and torsion angles (°) for **9**

P(1)–C(7)	1.792(3)
P(1)–C(2)	1.806(4)
P(1)–C(3)	1.830(3)
P(1)–B(1)	1.897(5)
C(7)–P(1)–C(2)	109.6(2)
C(7)–P(1)–C(3)	111.2(2)
C(2)–P(1)–C(3)	96.0(2)
C(7)–P(1)–B(1)	116.5(2)
C(2)–P(1)–B(1)	108.9(2)
C(3)–P(1)–B(1)	112.9(2)
B(1)–P(1)–C(7)–C(12)	26.9(4)
C(2)–P(1)–C(3)–C(4)	23.6(3)
C(3)–P(1)–C(2)–C(1)	−26.6(2)

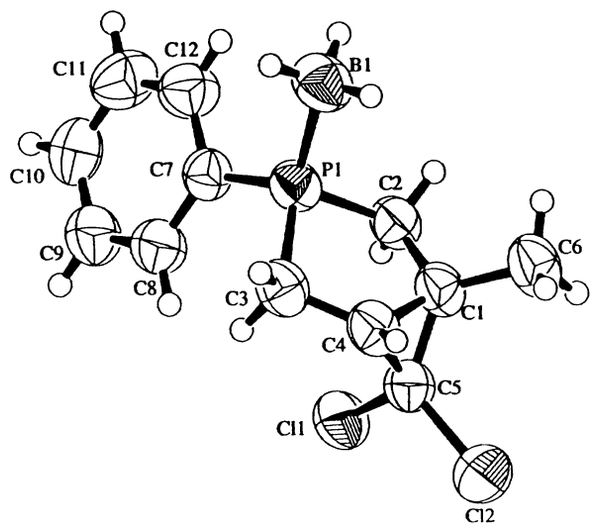
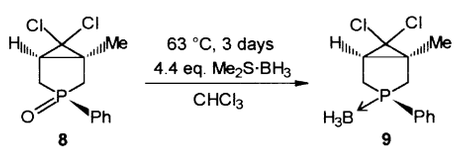


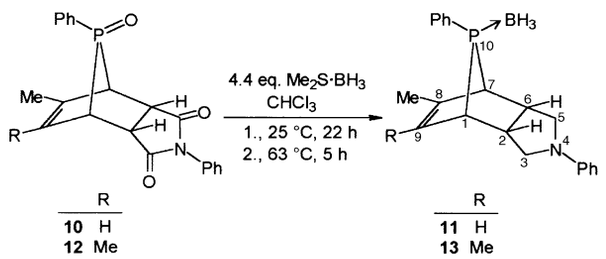
Fig. 2 Perspective view of **9**; hydrogen atoms are shown, but not labeled.



Scheme 4

From the above observations it is clear that the ring strain of the starting cyclic phosphine oxide is critical; the P=O group of strained tetrahydro- and dihydrophospholes (**1** and **3**) can be converted to a P→BH_3 function, at the same time, the

phosphinane oxides (*e.g.* **5**), obviously lacking any considerable ring strain, resist the refunctionalisation effect of borane. It is, however, worth mentioning that while the conversion of the phosphole oxide derivatives (*e.g.* **1** or **3**) required forcing reaction conditions (a considerable excess of the borane and prolonged reaction times), the transformation of the more strained phosphole oxide dimers proceeded with a relative ease.[11] We wished to evaluate if phosphabicyclo[2.2.1]heptene derivatives, such as **10** and **12**, could also be converted readily to the corresponding boranes. We found that the use of 4.4 equivalents of the borane under mild conditions (1., 22 h at 25 °C, 2., 5 h at 63 °C) led to boranes **11** and **13** (Scheme 5).



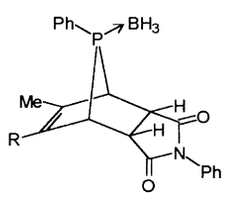
R	
10	H
12	Me

R	
11	H
13	Me

Scheme 5

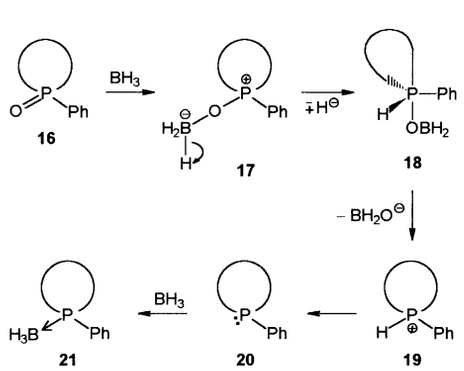
It is interesting that both imide carbonyl groups were reduced to methylene moieties. The boranes (**11** and **13**) were characterised by ^{31}P, ^{13}C and ^{11}B NMR, as well as FAB-MS. The molecular ions for compounds **11** and **13** appeared in unprotonated forms.

The use of less than 4.4 equivalents of the borane (3 equivalents) led to mixtures containing predominantly **11** (or **13**) and only a little amount of the expected product **14** (or **15**) was formed, as shown by ^{31}P NMR and FAB-MS.[16]



R	
14	H
15	Me

The first step of the above transformations is probably the nucleophilic attack of the oxygen atom of the P=O group in **16** on the boron atom of the borane to afford species **17** which is stabilised by a hydride anion shift. The key intermediate (**18**) so formed with a pentacoordinate phosphorus atom and with a trigonal bipyramidal geometry loses the elements of BH_2OH resulting in the formation of phosphine **20** and then final product **21** by reaction with the excess of borane (Scheme 6).



Scheme 6

Only a single example, the deoxygenation of triphenylphosphine oxide, is known from the literature for the reduction of phosphine oxides to phosphines by borane.[17] The deoxygenation of phosphine oxides by different silanes,[14] and quite recently by alanes,[18,19] is, however, a well-known method. This is the first time that phosphine oxides have been converted under relatively mild conditions (63 °C) to the boranes by borane, moreover in a one-pot manner. The synthesis described earlier uses trialkylamine–boranes and a reaction temperature higher than 120 °C.[17] Unfortunately, no details of the experimental procedure and the yield were provided. In our case, the only requirement is that the starting cyclic phosphine oxide should have a notable ring strain. For the phosphabicyclo[2.2.1]-heptenes, a C–P–C angle of *ca.* 83.0° was reported.[20] The driving force for the deoxygenation is the decrease of the ring strain in five-coordinate intermediate **18**. The example of the conversion of triphenylphosphine oxide to triphenylphosphine–borane by borane ($T \geq 120$ °C)[17] shows clearly the effect of the lack of ring strain in the starting *P*-oxide.

The complete reduction of an imide (or amide) function under the conditions of the reaction with borane is unusual and hence is of novelty.

It can be concluded that cyclic phosphine oxides, such as dihydro- and tetrahydrophosphole 1-oxides, as well as phosphabicyclo[3.1.0]hexane 3-oxides and phosphabicyclo[2.2.1]-heptene 7-oxides can be efficiently transformed to the corresponding phosphine–boranes by reaction with 4.4 equivalents of borane in a one-pot synthesis. The only criterion of the novel refunctionalisation taking place through a pentacoordinate P-intermediate is that the starting heterocycle should be of considerable ring strain. The P=O ⟶ P→BH_3 transformation can probably be extended to non-cyclic compounds provided that an elevated reaction temperature is applied. This is the first case that simple cyclic phosphine–boranes have been characterised by single crystal X-ray analysis.

Experimental

The ^{31}P, ^{13}C, ^{1}H and ^{11}B NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, 500 and 160.4 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4, TMS or $F_3B{\cdot}OEt_2$. The couplings are given in Hz. EI-mass spectra were obtained on a MS-902 spectrometer at 70 eV. FAB measurements were conducted on a reverse geometry VG ZAB-2SEQ instrument using a 30 kV Cs^+ ion gun and 8 kV accelerating voltage.

Preparation of the starting materials

Tetrahydrophosphole oxide **1** was obtained by the catalytic hydrogenation of the dihydro derivative **3** (1.8 g, 8.74 mmol) at 50 °C and 11 bar in methanol (50 mL) using 10% Pd/C (0.9 g) and by subsequent purification by column chromatography (silica gel, 2% methanol in chloroform). Yield: 1.2 g (66%) of **1**; ^{31}P NMR ($CDCl_3$) δ 59.4; MS, *m*/*z* (rel. int.) 208 (M^+, 100), 193 (M − Me, 36), 125 (PhPO + H, 63); $M^+_{found} = 208.0995$, $C_{12}H_{17}OP$ requires 208.1017.

Phosphinane oxide **5** and phosphabicyclo[3.1.0]hexane **8** were prepared as described earlier.[21,22]

Phosphabicyclo[2.2.1]heptene **12** was synthesized according to an earlier procedure.[23] Compound **10** was prepared in a similar way *via* the trapping of 3-methyl-1-phenylphosphole 1-oxide (0.013 mmol) by *N*-phenylmaleimide (5.0 g, 0.029 mmol) at 60 °C. The phosphole oxide was generated *in situ* from 3,4-dibromo-3-methyl-1-phenyltetrahydrophosphole oxide (4.57 g, 0.013 mmol) by triethylamine (4.4 mL, 0.032 mmol) in benzene (100 mL) solution. Flash column chromatography (silica gel, 3% methanol in chloroform) of the crude product obtained after the evaporation of the filtrate afforded 1.14 g (25%) of **10**. ^{31}P NMR $CDCl_3$) δ 83.9; FAB, 364 (M + H); $(M + H)^+_{found} = 364.1072$, $C_{21}H_{19}NO_3P$ requires 364.1103.

General procedure for the synthesis of phosphine–boranes from the oxides

To 1.12 mmol of the phosphine oxide (**1**, **8**, **10** and **12**) in 20 mL of absolute chloroform was added 4.4 equivalents (2.5 mL) of 2 M dimethyl sulfide–borane in THF, and the solution was stirred at 25–63 °C for 27–72 h as shown in Schemes 1, 4 and 5, respectively. After the addition of 2.0 mL of water, the mixture was stirred for 10 min and then filtered. The organic phase of the filtrate was separated and dried (Na_2SO_4). The crude product obtained after evaporating the volatile components was purified by column chromatography (silica gel, 2% methanol in chloroform) to give the products (**2**, **9**, **11** and **13**) as crystalline or semicrystalline solids. The purity of the phosphine–boranes (**2**, **9**, **11** and **13**) was indicated by TLC.

3,4-Dimethyl-1-phenyl-2,3,4,5-tetrahydrophosphole–borane 2. Yield: 92%, mp 54–55 °C; ^{31}P NMR ($CDCl_3$) δ 28.3; ^{11}B NMR ($CDCl_3$) δ −33.8; ^{13}C NMR ($CDCl_3$) δ 15.9 (J = 5.6, Me), 33.0 (J = 35.6, C_2), 39.6 (C_3), 128.8 (J = 9.6, $C_{3'}$*), 131.0 (J = 2.0, $C_{4'}$), 131.2 (J = 8.7, $C_{2'}$*), 132.0 (J = 47.1, $C_{1'}$), *may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.06 (d, J = 6.7, 6H, Me), 1.88–1.97 (m, 2H, CH), 2.14–2.23 (m, 2H, CH), 2.40–2.52 (m, 2H, CH), 7.40–7.77 (m, 5H, Ar); MS, *m*/*z* (rel. int.) 192 (M − BH_3, 100), 177 (192 − Me, 12).

6,6-Dichloro-1-methyl-3-phenyl-3-phosphabicyclo[3.1.0]-hexane(*P*–*B*)borane 9. Yield: 65%, mp 98–100 °C; ^{31}P NMR ($CDCl_3$) δ 59.1 (J_{PB} = 60.5), lit.[4] δ 59.0 (J_{PB} = 64.7); MS, *m*/*z* 271 (M^+ − H).

8-Methyl-4,10-diphenyl-4-aza-10-phosphabicyclo[5.2.1.0^{2,6}]-dec-8-ene(*P*–*B*)borane 11. Yield: 45%; ^{31}P NMR ($CDCl_3$) δ 130.6; ^{11}B NMR ($CDCl_3$) δ −35.2; ^{13}C NMR ($CDCl_3$) δ 20.6 (Me), 42.6 (J = 18.0, C_2^a), 42.9 (J = 17.2, C_6^a), 44.1 (J = 33.4, C_1), 48.9 (J = 33.2, C_7), 51.0 (J = 11.2, C_5^b), 51.4 (J = 10.8, C_3^b), 112.8 ($C_{3''}$), 116.7 ($C_{4''}$), 125.4 (C_9), 128.5 (J = 9.2, $C_{3'}^c$), 129.2 ($C_{2''}$), 130.7 ($C_{4'}$), 132.0 (J = 8.0, $C_{2'}^c$), 143.9 (C_8), [a–c]may be reversed; ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3H, Me), 2.96–3.41 (m, 4H, e), 3.48–3.59 (m, 2H, e), 3.79–3.93 (m, 2H, e), 6.71 (dd, J_1 = J_2 = 7.2, 1H, C_9-H), 7.17–7.52 (m, 10H, Ar), [e]skeletal hydrogen atom(s); FAB, 333 (M); M^+_{found} = 333.1783, $C_{21}H_{25}BNP$ requires 333.1818 for the ^{11}B isotope.

8,9-Dimethyl-4,10-diphenyl-4-aza-10-phosphabicyclo-[5.2.1.0^{2,6}]dec-8-ene(*P*–*B*)borane 13. Yield: 39%; ^{31}P NMR ($CDCl_3$) δ 124.4; ^{11}B NMR ($CDCl_3$) δ −34.9; ^{13}C NMR ($CDCl_3$) δ 17.1 (Me), 42.5 (J = 18.1, C_2), 49.2 (J = 33.8, C_1), 50.8 (J = 11.3, C_5), 112.8 ($C_{3''}$), 116.6 ($C_{4''}$), 128.3 (J = 10.1, $C_{3'}$*), 129.1 ($C_{2''}$), 130.5 ($C_{4'}$), 131.3 (J = 7.5, $C_{2'}$*), 133.8 (C_4), *may be reversed; FAB, 347 (M); M^+_{found} = 347.1947, $C_{22}H_{27}BNP$ requires 347.1974 for the ^{11}B isotope.

Phosphine–boranes 4, 2 and 2′. These were obtained from the reaction of 2,5-dihydrophosphole oxide **3** with dimethyl sulfide–borane. The reaction was carried out according to the General Procedure and Scheme 2 to afford a mixture consisting of 27% of product **4** (δ_P = 21.8, M + H = 205), 40% of compound **2** (δ_P = 28.9, M + H = 207) and 33% of isomer **2′** (δ_P = 29.5, M + H = 207).

3-Methyl-1-phenylphosphinane–borane 6. To 0.5 g (2.40 mmol) of phosphine oxide **5** consisting of a 70 : 30 mixture of isomers in 25 mL of benzene was added 0.64 mL (7.92 mmol) of pyridine and 0.27 mL (2.64 mmol) of trichlorosilane, and the mixture was stirred at the boiling point under a nitrogen atmosphere for 8 h. The contents of the flask were filtered and the filtrate evaporated, finally under high vacuum, to leave an oily residue of phosphine **7** in quantitative yield. Intermediate **7** so obtained was dissolved in 20 mL of chloroform and treated with 1.4 mL of 2 M dimethyl sulfide–borane in THF (2.80 mmol) at room temperature. After a 2 h reaction time, 1.0 mL of water was added and the mixture stirred for 5 min. The precipitated material was removed by filtration and the organic phase dried (Na_2SO_4). The crude product obtained after evaporating the volatile components of the filtrate was purified by column chromatography (2% methanol in chloroform, silica gel) to give 0.20 g (41%) of borane **6** as a 55 : 45 mixture of two isomers; FAB, 207 (M + H); $(M + H)^+_{found}$ = 207.1454, $C_{12}H_{21}BP$ requires 207.1474 for the ^{11}B isotope.

6$_1$. ^{31}P NMR ($CDCl_3$) δ 9.1; ^{11}B NMR ($CDCl_3$) δ −33.2; ^{13}C NMR ($CDCl_3$) δ 21.3 (J = 35.1, C_6), 21.6 (J = 7.5, C_5), 24.8 (J = 10.7, Me), 28.5 (J = 7.1, C_3), 30.0 (J = 33.8, C_2), 34.9 (J = 3.6, C_4), 129.1 (J = 8.9, $C_{3'}$*), 129.2 (J = 50.5, $C_{1'}$), 130.5 (J = 2.0, $C_{4'}$), 130.8 (J = 8.3, $C_{2'}$*), *may be reversed.

6$_2$. ^{31}P NMR ($CDCl_3$) δ 4.8; ^{11}B NMR ($CDCl_3$) δ −37.9; ^{13}C NMR ($CDCl_3$) δ 22.0 (J = 2.1, C_5), 23.0 (J = 34.7, C_6), 24.9 (J = 13.5, Me), 29.2 (C_3), 31.8 (J = 33.5, C_2), 35.6 (J = 4.7, C_4), 128.9 (J = 9.7, $C_{3'}$*), 131.3 (J = 2.4, $C_{4'}$), 131.3 (J = 8.4, $C_{2'}$*), *may be reversed.

Crystal data for 2 and 9†

X-Ray diffraction data of single crystals of **2** and **9** were collected at 293 K.

Crystal data for **2**: $C_{12}H_{20}BP$, M = 206.06, triclinic, space group $P\bar{1}$, a = 9.361(6) Å, b = 11.236(6) Å, c = 6.912(2) Å, α = 104.73(3)°, β = 107.85(2)°, γ = 65.89(2)°, V = 624.6(5) Å^3, Z = 2, D_c = 1.096 g cm^{-1}, μ(Mo-Kα) = 0.182 mm^{-1}.

Crystal data for **9**: $C_{12}H_{16}BCl_2P$, M = 272.93, monoclinic, space group $P2_1/n$, a = 6.851(2) Å, b = 17.570(4) Å, c = 11.462(3) Å, β = 103.59(4)°, V = 1341.0(5) Å^3, Z = 4, D_c = 1.352 g cm^{-1}, μ(Mo–Kα) = 0.573 mm^{-1}.

Structure solutions with direct methods were carried out with the teXsan package.[24] Refinements were carried out using the SHELXL-93 program.[25] Final R indices for **2** are R = 0.1213, R_w = 0.2613 (for 1394 unique reflections) R = 0.0757, R_w = 0.1990 ($I > 2\sigma(I)$); those for **9** are R = 0.0700, R_w = 0.1494 (for 1518 unique reflections) R = 0.0465, R_w = 0.1238 ($I > 2\sigma(I)$). Final difference maps: 0.365 and −0.398 e Å^{-3} for **2**; 0.389 and −0.340 e Å^{-3} for **9**.

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For **15**: ^{31}P NMR ($CDCl_3$) δ 125.4; FAB-MS, 376 (M + H); $(M + H)^+_{found}$ = 376.1600, $C_{22}H_{24}BNO_2P$ requires 376.1638 for the ^{11}B isotope.
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