

# Convenient Mild and Selective Hydrophosphination of Functionalized Alkenes: Access to P,O and P,S Derivatives

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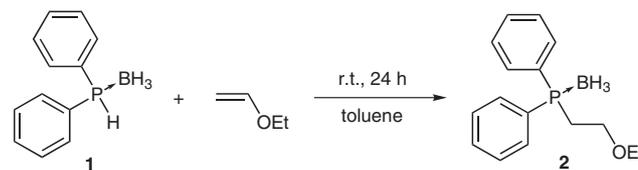
**Abstract:** The synthesis of new functionalized phosphines is carried out through the easy and atom economic hydrophosphination reaction of functionalized alkenes such as vinyl ethers and vinyl thioethers. The reactions occur under mild conditions without catalyst using phosphine-boranes as hydrophosphinating agents.

**Key words:** addition reactions, alkenes, boron, phosphorus, radical reactions

Phosphines are important ligands in transition-metal-catalyzed reactions.<sup>1</sup> Among the variety of methods employed for their synthesis, hydrophosphination (i.e., the addition of a P–H bond to an unsaturation) is a straightforward and efficient process, which fulfils the atom economy principle. The main promoters used are metal complexes, strong bases, acids, and free radicals.<sup>2</sup> However, this approach continues to pose considerable challenges in the preparation of oxygen-sensitive phosphines. An alternate approach using phosphine-boranes as hydrophosphinating agent has solved a number of difficulties. Hence, the borane group acts as a protecting group and prevents the oxidation of the phosphine. It also activates through an inductive effect the P–H bond and consequently permits to perform the reactions under mild conditions or even in the absence of a catalyst.<sup>3,4</sup> Another advantage of the phosphine-boranes is related to the existence of efficient methods to remove the borane.<sup>5</sup> The hydrophosphination using phosphine-borane complexes has been largely used with simple unsaturated derivatives.<sup>3</sup> On the other hand, little is known about the hydrophosphination of functionalized derivatives<sup>3f,g,6</sup> despite the fact that it would give an easy entry to bifunctional phosphine ligands. Here, we report the hydrophosphination of vinyl ethers and vinyl thioethers, which are available substrates. No precedent dealing with the hydrophosphination of such substrates by phosphine-borane could be found in the literature.<sup>2</sup> The lack of examples may be related to the Lewis base character of the oxygen or sulfur atom, which could promote the decomplexation of the borane group and thus deprotect the phosphine-borane leading to an unactivated and unprotected phosphine.<sup>7</sup> Herein, we document for the first time results on the hydrophosphination of vinyl ethers and vinyl thioethers using secondary phosphine-boranes as hydrophosphinating agents. The compounds obtained could be of great interest for homogeneous catalysis as hemilabile ligands.<sup>8</sup>

The reaction conditions for the hydrophosphination of vinyl ethers were set using the couple diphenylphosphine-borane **1**/ethyl vinyl ether (Equation 1). To prevent decomplexation, the reaction was carried out using a low amount of an inert solvent (toluene) at ambient temperature without any catalyst. To our delight, the whole precursor **1** was consumed after 24 hours leading to phosphine-borane **2** as the main product (96%), the remaining percentage corresponding to the oxide of the decomplexed hydrophosphination product. This preliminary result shows that under these mild conditions, decomplexation of the phosphine-borane by the ether is rather low. It is also worth noting that no catalyst is required to promote the reaction.

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Equation 1

Only one regioisomer was detected by <sup>31</sup>P NMR spectroscopy. <sup>1</sup>H NMR revealed the exclusive formation of the anti-Markovnikov adduct **2**. The observed regioselectivity is similar to that obtained under radical activation with free phosphines.<sup>9</sup> However, in our system, only a slight excess (1.2 equiv) of alkenes was used instead of the 2 or 3 equivalents, which are required in radical-activated process. Moreover, the reaction requires neither thermal activation nor UV irradiation, thus avoiding the polymerization of the alkene. Finally, in contrast with 'free' phosphines, no workup was required. The adduct was easily purified in air by flash filtration on a pad of silica gel (flash chromatography using toluene as eluent) affording **2** in 76% yield. In the first trial, the reaction was carried out on a 100 mg precursor scale but the reaction can easily be scaled up to grams under the previously defined conditions. In this case, a strong improvement of the isolated yield is observed, indicating that the moderate yields, which are obtained with low amount of precursors, are inherent to the purification process and not to the conditions of the reaction.

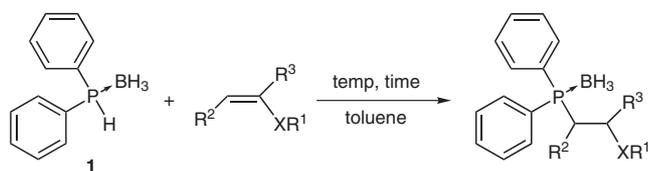
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As shown in Table 1, the methodology can be successfully applied to other acyclic and cyclic vinyl ethers. Butyl vinyl ether was totally hydrophosphinated in 24 hours while 2-methoxypropene required 96 hours for a full conversion (Equation 2, Table 1, entries 2, 3). As in the previous example, no competing decomplexation of the phosphine-borane was noticed. Tertiary phosphine-boranes **3** and **4** having a predictable regiochemistry (anti-Markovnikov adducts) were isolated in 74 and 60% yields, respectively, and fully characterized. With 3,4-dihydro-2*H*-pyran, no strong influence of the cyclic structure on the reactivity was observed and hydrophosphination could be carried out in 48 hours at room temperature. Regioselectively, the phosphorus atom enters exclusively at the carbon in the  $\beta$ -position producing as expected the phosphine-borane **5**, which was isolated in 69% yield after flash chromatography (Equation 2, Table 1, entry 4).



Equation 2

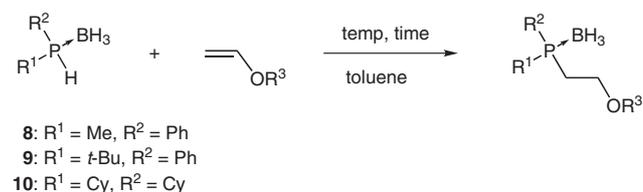
Table 1 Reaction of **1** with Vinyl Ethers and Thioethers

| Entry | X | R <sup>1</sup> | R <sup>2</sup> | R <sup>3</sup> | Temp (°C) | Time (h) | Yield (%) | Product  |
|-------|---|----------------|----------------|----------------|-----------|----------|-----------|----------|
| 1     | O | Et             | H              | H              | r.t.      | 24       | 76        | <b>2</b> |
| 2     | O | Bu             | H              | H              | r.t.      | 24       | 74        | <b>3</b> |
| 3     | O | Me             | H              | Me             | r.t.      | 96       | 60        | <b>4</b> |
| 4     |   |                |                |                | r.t.      | 48       | 69        | <b>5</b> |
| 5     | S | Et             | H              | H              | 35        | 24       | 69        | <b>6</b> |
| 6     | S | Ph             | H              | H              | 35        | 48       | 64        | <b>7</b> |

P,S ligands have a different behavior than P,O ligands due to the bulkiness of the sulfur atom and to its electronic properties, which makes sulfur a softer ligand, according to Pearson's theory.<sup>10</sup> We were consequently interested to check our method in the synthesis of such P,S derivatives. Ethyl vinyl sulfide was selected as a model substrate and reacted with **1** under the previously defined conditions for the oxygenated counterpart (24 h, r.t.). However, the conversion remained low (58%). Upon slightly increasing the temperature to 35 °C, an almost complete conversion was obtained after 24 hours. Again, as with vinyl ethers, no decomplexation of the phosphine borane was noticed and only the anti-Markovnikov regioisomer was formed.<sup>11</sup> Phosphine-borane **6** was isolated after purification in 69% yield (Equation 2, Table 1, entry 5). With phenyl vinyl sulfide, the hydrophosphination was complete at 35 °C in

48 hours affording phosphine-borane **7** in 64% yield after purification (Equation 2, Table 1, entry 6).

All the substrates being easily hydrophosphinated by **1** under mild conditions (r.t. or 35 °C), we then extended our study to more electron-rich phosphine precursors, which are known to be less reactive than diarylphosphine derivatives.<sup>3</sup> Methylphenylphosphine-borane **8** was first selected. Addition of **8** to ethyl vinyl ether was performed at room temperature. The reaction was completed in 24 hours and phosphine-borane **11** was isolated in 73% yield (Equation 3, Table 2, entry 1).



Equation 3

Table 2 Reaction of Phosphine-boranes **8–10** with Vinyl Ethers

| Entry          | Precursor | R <sup>3</sup> | Temp (°C) | Time   | Yield (%)       | Product   |
|----------------|-----------|----------------|-----------|--------|-----------------|-----------|
| 1              | <b>8</b>  | Et             | r.t.      | 24 h   | 73              | <b>11</b> |
| 2              | <b>9</b>  | Et             | r.t.      | 7 d    | 47              | <b>12</b> |
| 3              | <b>10</b> | Bu             | 70        | 48 h   | 22              | <b>13</b> |
| 4 <sup>a</sup> | <b>10</b> | Bu             | 75        | 30 min | 14              | <b>13</b> |
| 5              | <b>10</b> | Bu             | r.t.      | 96 h   | 54 <sup>b</sup> | <b>13</b> |
| 6              | <b>10</b> | Et             | r.t.      | 96 h   | 53 <sup>b</sup> | <b>14</b> |

<sup>a</sup> Microwave activation.

<sup>b</sup> Amount of Et<sub>3</sub>B used: 1.2 equiv.

The reactivity of *tert*-butylphenylphosphine-borane **9** was, as expected, lower due to the steric bulkiness of the *tert*-butyl group. Nevertheless, after seven days at room temperature, hydrophosphination product **12** could be isolated in a reasonable yield of 47% (Equation 3, Table 2, entry 2). Finally, we selected dicyclohexylphosphine-borane **10** as precursor. It soon became obvious that the conditions defined for phosphines **2**, **8**, and **9** were inappropriate with such a bulky and electron-rich phosphine. Hence after four days at room temperature, no hydrophosphination product was observed with ethyl vinyl ether. Former studies on the hydrophosphination of alkenes with such phosphine derivatives showed that the reaction required a thermal activation.<sup>3b,f</sup> Ethyl vinyl ether having a low boiling point (bp 36 °C), we turned to butyl vinyl ether, which was more adapted for a thermal activation (bp 94 °C). Various temperatures were tested without success. Only high temperature (70 °C, 48 h) afforded some hydrophosphination product **13** although in a rather low amount (36%), as determined by <sup>31</sup>P NMR spectroscopy. The expected product was accompanied by various side-

products and phosphine-oxides indicating decomplexation of phosphine-borane derivatives. Nevertheless, phosphine **13** was isolated in 22% yield (Equation 3, Table 2, entry 3). To improve the yield we used a microwave irradiation (MWI) device. Former studies had shown the compatibility of this device with phosphine-boranes and its advantage with bulky and electron-rich hydrophosphinating agents.<sup>3b,c,e,f</sup> However, the reaction afforded mainly decomplexed and oxidized secondary phosphines. The expected adduct **13** was isolated only in low yield (14%) (Equation 3, Table 2, entry 4). These last results show the importance of avoiding high temperature in order to limit the decomplexation-oxidation of phosphine-boranes and the formation of side-products when using ethers as substrates.<sup>12</sup>

Since thermal activation was inappropriate, our next study focused on the use of a radical activator. This choice was based on the fact that: i) we had previously proposed that the mechanism of the uncatalyzed hydrophosphination reaction using phosphine-borane derivatives could involve a radical intermediate,<sup>3b,c</sup> and ii) a radical mechanism was recently proposed for the addition of phosphate oxides to alkenes in the presence of a catalytic amount of oxygen.<sup>13</sup> To prevent the formation of side-products and the polymerization of the alkenes, we avoided AIBN, which requires the use of a high temperature (65–70 °C) and selected Et<sub>3</sub>B as a radical initiator. Trialkylboranes and especially Et<sub>3</sub>B have been widely used as low temperature initiators.<sup>14</sup> To the best of our knowledge, they were never employed with phosphine-borane derivatives although they have been used in one report dealing with C–P bond formation by hydrophosphination using hypophosphite as hydrophosphinating agent.<sup>15</sup> Et<sub>3</sub>B in hexane (1.2 equiv) was simply added to the reaction mixture and the reaction was run at room temperature using a 1:1.2 ratio of phosphine-borane **10**/butyl vinyl ether in a small amount of toluene. Under these conditions, the reaction was complete in 96 hours at room temperature and compound **13** was isolated in 54% yield (Equation 3, Table 2, entry 5). To verify that the reaction was indeed radical activated, the experiment was repeated in the presence of a radical trap (duroquinone). After 24 hours, secondary phosphine-borane **10** was recovered unreacted and no trace of phosphine-borane **13** was detected by <sup>31</sup>P NMR spectroscopy, confirming the radical activation induced by Et<sub>3</sub>B. The reaction was next carried out with ethyl vinyl ether in the presence of Et<sub>3</sub>B, and **14** was isolated in 53% yield (Equation 3, Table 2, entry 6). The Et<sub>3</sub>B activation was also observed, although less impressive, in the reaction between butyl vinyl ether and phosphine-borane **1**, the reaction being completed in 13 hours compared to 24 hours in the absence of the radical catalyst. All these results are in agreement with a radical-catalyzed process.

In summary, we have devised a fully regioselective hydrophosphination of functionalized alkenes, which gives an efficient and easy access to a new family of ether and thioether/phosphine-borane derivatives. All the reactions were carried out under mild conditions (r.t. to 35 °C) and

do not require any catalyst except for the very bulky and electron-rich dicyclohexylphosphine-borane, where a radical activation using Et<sub>3</sub>B was applied at room temperature. Application in homogeneous catalysis of the potential phosphine-ether ligands, which have been prepared by this methodology, is under investigation.

Phosphine-boranes **1**,<sup>16</sup> **8**,<sup>17</sup> **9**,<sup>18</sup> and **10**<sup>19</sup> were synthesized following published procedures. Toluene was dried by an Innovative Technology Pure Solvent device. Solvents used for column chromatography were directly used from commercial bottles. The microwave irradiation apparatus was a Discover from CEM Company with a maximal power of 300 watts.

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Bruker DPX 250 and Bruker AC 400 spectrometers. <sup>11</sup>B NMR spectra were recorded on a Bruker AC 400 spectrometer. TMS was used as internal reference for recording the <sup>1</sup>H and <sup>13</sup>C NMR spectra. 85% H<sub>3</sub>PO<sub>4</sub> and BF<sub>3</sub>·OEt<sub>2</sub> were used as external reference for <sup>31</sup>P and <sup>11</sup>B NMR spectroscopy, respectively. Coupling constants are reported in Hz. Mass spectra were recorded on Varian MAT 311 and Varian Saturn 2000 spectrometers in high-resolution mode.

### Uncatalyzed Hydrophosphination of Vinyl Derivatives; General Procedure

An oven-dried Schlenk-tube was charged with phosphine-borane precursor **1**, **8** or **9** (1 equiv). After three cycles with oil pump vacuum/N<sub>2</sub> purge, the respective alkene (1.2 equiv) was added under a N<sub>2</sub> flow. Then, toluene (0.25 mL) was added to the solution. The mixture was stirred for the time and at temperature indicated in Tables 1 and 2, and then cooled to r.t. as required. The crude product was directly purified by silica gel chromatography. The pure product was obtained after drying under vacuum.

### Et<sub>3</sub>B-Catalyzed Hydrophosphination of Vinyl Derivatives with **10**; General Procedure

An oven-dried Schlenk-tube was charged with phosphine-borane precursor **10** (1 equiv). After three cycles with oil pump vacuum/N<sub>2</sub> purge, the respective alkene (1.2 equiv) was added under a N<sub>2</sub> flow. Then, toluene (0.25 mL) and Et<sub>3</sub>B (1.2 equiv) were added to the solution. The mixture was stirred for 96 h at r.t. The crude product was directly purified by silica gel chromatography. The product was obtained after drying under vacuum.

### (2-Ethoxy)ethylidiphenylphosphine-borane (**2**)

Prepared from phosphine-borane **1** (100 mg, 0.5 mmol) and ethyl vinyl ether (58 μL, 0.6 mmol); yield: 76%, translucent oil; *R*<sub>f</sub> = 0.35 (toluene).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.75–7.72 (m, 1 H), 7.72–7.68 (m, 2 H), 7.68–7.64 (m, 1 H), 7.56–7.37 (m, 6 H), 3.65 (dt, <sup>3</sup>*J*<sub>H,P</sub> = 15.2 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, 2H), 3.41 (q, <sup>3</sup>*J*<sub>H,H</sub> = 7.0 Hz, 2 H), 2.60 (dt, <sup>2</sup>*J*<sub>H,P</sub> = 11.4 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, 1 H), 2.55 (dt, <sup>2</sup>*J*<sub>H,P</sub> = 11.4 Hz, <sup>3</sup>*J*<sub>H,H</sub> = 7.5 Hz, 1 H), 1.096 (t, <sup>3</sup>*J*<sub>H,H</sub> = 7.0 Hz, 3 H), 0.90 (qm, <sup>1</sup>*J*<sub>H,B</sub> = 90.1 Hz, 3 H).

<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>): δ = 132.1 (d, <sup>2</sup>*J*<sub>C,P</sub> = 9.4 Hz), 131.2 (d, <sup>4</sup>*J*<sub>C,P</sub> = 1.9 Hz), 129.3 (d, <sup>1</sup>*J*<sub>C,P</sub> = 56.6 Hz), 128.8 (d, <sup>3</sup>*J*<sub>C,P</sub> = 10.1 Hz), 66.3 (s), 64.9 (d, <sup>2</sup>*J*<sub>C,P</sub> = 5.0 Hz), 26.4 (d, <sup>1</sup>*J*<sub>C,P</sub> = 36.48 Hz), 15.0 (s).

<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>): δ = 13.53 (dm, <sup>1</sup>*J*<sub>P,B</sub> = 71.0 Hz).

HRMS: *m/z* calcd for [M – H]<sup>+</sup>: 258.1174; found: 258.1182.

### (2-Butoxy)ethylidiphenylphosphine-borane (**3**)

Prepared from phosphine-borane **1** (100 mg, 0.5 mmol) and butyl vinyl ether (78 μL, 0.6 mmol); yield: 74%; translucent oil; *R*<sub>f</sub> = 0.2 (toluene).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.75\text{--}7.72$  (m, 1 H),  $7.72\text{--}7.68$  (m, 2 H),  $7.68\text{--}7.65$  (m, 1 H),  $7.54\text{--}7.39$  (m, 6 H),  $3.65$  (dt,  $^3J_{\text{H,P}} = 16.0$  Hz,  $^3J_{\text{H,H}} = 7.4$  Hz),  $6.43$  (t,  $^3J_{\text{H,H}} = 6.4$  Hz, 2 H),  $2.59$  (dt,  $^2J_{\text{H,P}} = 11.5$  Hz,  $^3J_{\text{H,H}} = 7.4$  Hz, 1 H),  $2.55$  (dt,  $^2J_{\text{H,P}} = 11.5$  Hz,  $^3J_{\text{H,H}} = 7.4$  Hz, 1 H),  $1.52\text{--}1.36$  (m, 2 H),  $1.36\text{--}1.16$  (m, 2 H),  $0.86$  (t,  $^3J_{\text{H,H}} = 7.2$  Hz, 3 H),  $0.70\text{--}0.10$  (m, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 132.1$  (d,  $^2J_{\text{C,P}} = 9.4$  Hz),  $131.2$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $129.4$  (d,  $^1J_{\text{C,P}} = 56.0$  Hz),  $128.8$  (d,  $^3J_{\text{C,P}} = 10.1$  Hz),  $70.8$  (s),  $65.2$  (d,  $^2J_{\text{C,P}} = 5.0$  Hz),  $31.7$  (s),  $26.4$  (d,  $^1J_{\text{C,P}} = 36.5$  Hz),  $19.2$  (s),  $13.9$  (s).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.72$  (dm,  $^1J_{\text{P,B}} = 72.0$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{BH}_3]^+$ : 286.1487; found: 286.1492.

#### [(2-Methoxy)-2-methyl]ethyldiphenylphosphine-borane (4)

Prepared from phosphine-borane **1** (100 mg, 0.5 mmol) and 2-methoxypropene (58  $\mu\text{L}$ , 0.6 mmol); yield: 60%; translucent oil;  $R_f = 0.3$  (toluene).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79\text{--}7.64$  (m, 4 H),  $7.53\text{--}7.37$  (m, 6 H),  $3.84\text{--}3.67$  (m, 1 H),  $3.13$  (s, 3 H),  $2.67$  (ddd,  $^2J_{\text{H,H}} = 14.5$  Hz,  $^2J_{\text{H,P}} = 13.3$  Hz,  $^3J_{\text{H,H}} = 7.3$  Hz, 1 H),  $2.24$  (ddd,  $^2J_{\text{H,H}} = 14.5$  Hz,  $^2J_{\text{H,P}} = 9.3$  Hz,  $^3J_{\text{H,H}} = 5.3$  Hz, 1 H),  $1.18$  (dd,  $^3J_{\text{H,H}} = 6.1$  Hz,  $^4J_{\text{H,P}} = 1.1$  Hz, 3 H),  $0.98$  (qm,  $^1J_{\text{H,B}} = 106.1$  Hz, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 132.5$  (d,  $^2J_{\text{C,P}} = 9.4$  Hz),  $132.2$  (d,  $^2J_{\text{C,P}} = 8.8$  Hz),  $131.2$  (d,  $^4J_{\text{C,P}} = 1.9$  Hz),  $131.1$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $130.5$  (d,  $^1J_{\text{C,P}} = 56.6$  Hz),  $130.0$  (d,  $^1J_{\text{C,P}} = 56.0$  Hz),  $128.9$  (d,  $^3J_{\text{C,P}} = 10.1$  Hz),  $128.7$  (d,  $^3J_{\text{C,P}} = 10.1$  Hz),  $73.0$  (s),  $56.0$  (s),  $33.9$  (d,  $^1J_{\text{C,P}} = 35.9$  Hz),  $20.9$  (d,  $^3J_{\text{C,P}} = 8.2$  Hz).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 14.43$  (dm,  $^1J_{\text{P,B}} = 70.7$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{H}]^+$ : 271.1423; found: 271.1436.

#### Pyran-2-ylidiphenylphosphine-borane (5)

Prepared from phosphine-borane **1** (100 mg, 0.5 mmol) and 3,4-dihydro-2H-pyran (55  $\mu\text{L}$ , 0.6 mmol); yield: 69%; translucent oil;  $R_f = 0.3$  (toluene).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.83\text{--}7.66$  (m, 4 H),  $7.57\text{--}7.40$  (m, 6 H),  $4.01\text{--}3.90$  (m, 1 H),  $3.90\text{--}3.79$  (m, 1 H),  $3.59$  (dt,  $^5J_{\text{H,P}} = 2.0$  Hz,  $^3J_{\text{H,H}} = 11.25$  Hz, 1 H),  $3.40$  (dt,  $^5J_{\text{H,P}} = 3.25$  Hz,  $^3J_{\text{H,H}} = 11.0$  Hz, 1 H),  $2.89\text{--}2.68$  (m, 1 H),  $1.87\text{--}1.54$  (m, 4 H),  $1.70\text{--}0.15$  (m, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 132.6$  (d,  $^2J_{\text{C,P}} = 8.8$  Hz),  $132.4$  (d,  $^2J_{\text{C,P}} = 8.8$  Hz),  $131.6$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $131.5$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $129.1$  (d,  $^3J_{\text{C,P}} = 9.4$  Hz),  $129.0$  (d,  $^3J_{\text{C,P}} = 9.4$  Hz),  $127.6$  (d,  $^1J_{\text{C,P}} = 54.7$  Hz),  $127.5$  (d,  $^1J_{\text{C,P}} = 54.1$  Hz),  $68.4$  (s),  $68.2$  (d,  $^2J_{\text{C,P}} = 8.7$  Hz),  $32.7$  (d,  $^1J_{\text{C,P}} = 34.3$  Hz),  $29.9$  (s),  $26.5$  (d,  $^2J_{\text{C,P}} = 9.9$  Hz),  $24.1$  (s).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 16.63$  (dm,  $^1J_{\text{P,B}} = 61.5$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{H}]^+$ : 283.1423; found: 283.1414.

#### (2-Mercaptoethyl)ethyldiphenylphosphine-borane (6)

Prepared from phosphine-borane **1** (100 mg, 0.5 mmol) and ethyl vinyl sulfide (61  $\mu\text{L}$ , 0.6 mmol); yield: 69%; translucent oil;  $R_f = 0.65$  (toluene).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.75\text{--}7.62$  (m, 4 H),  $7.58\text{--}7.40$  (m, 6 H),  $2.72\text{--}2.64$  (m, 2 H),  $2.56$  (q,  $^3J_{\text{H,H}} = 7.4$  Hz, 2 H),  $2.55\text{--}2.47$  (m, 2 H),  $1.23$  (t,  $^3J_{\text{H,H}} = 7.4$  Hz, 3 H),  $1.02$  (qm,  $^1J_{\text{H,B}} = 81.4$  Hz, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 132.5$  (d,  $^2J_{\text{C,P}} = 8.8$  Hz),  $131.8$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $129.4$  (d,  $^3J_{\text{C,P}} = 9.5$  Hz),  $129.2$  (d,  $^1J_{\text{C,P}} = 54.8$  Hz),  $27.0$  (d,  $^1J_{\text{C,P}} = 32.7$  Hz),  $26.2$  (s),  $25.4$  (d,  $^2J_{\text{C,P}} = 2.0$  Hz),  $15.0$  (s).

$^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ ):  $\delta = 15.34$  (dm,  $^1J_{\text{P,B}} = 65.2$  Hz).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ ):  $\delta = -37.15$  (dq,  $^1J_{\text{P,B}} = 65.2$  Hz,  $^1J_{\text{B,H}} = 81.4$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{H}]^+$ : 287.1195; found: 287.1182.

#### (2-Mercaptophenyl)ethyldiphenylphosphine-borane (7)

Prepared from phosphine-borane **1** (100 mg, 0.5 mmol) and phenyl vinyl sulfide (79  $\mu\text{L}$ , 0.6 mmol); yield: 64%; translucent oil;  $R_f = 0.7$  (toluene).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.65\text{--}7.48$  (m, 4 H),  $7.48\text{--}7.27$  (m, 6 H),  $7.27\text{--}6.95$  (m, 5 H),  $3.02\text{--}2.89$  (m, 2 H),  $2.49\text{--}2.34$  (m, 2 H),  $0.92$  (qm,  $^1J_{\text{H,B}} = 82.5$  Hz, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 134.9$  (s),  $132.2$  (d,  $^2J_{\text{C,P}} = 9.4$  Hz),  $131.6$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $129.7$  (s),  $129.3$  (s),  $129.1$  (d,  $^3J_{\text{C,P}} = 10.1$  Hz),  $128.7$  (d,  $^1J_{\text{C,P}} = 55.3$  Hz),  $126.7$  (s),  $27.3$  (d,  $^2J_{\text{C,P}} = 2.5$  Hz),  $26.1$  (d,  $^1J_{\text{C,P}} = 32.1$  Hz).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 16.20$  (dm,  $^1J_{\text{P,B}} = 67.0$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{BH}_3 + \text{H}]^+$ : 323.1023; found: 323.1022.

#### (2-Ethoxy)ethylmethylphenylphosphine-borane (11)

Prepared from phosphine-borane **8** (70  $\mu\text{L}$ , 0.5 mmol) and ethyl vinyl ether (58  $\mu\text{L}$ , 0.6 mmol); yield: 73%; translucent oil;  $R_f = 0.7$  ( $\text{CH}_2\text{Cl}_2$ ).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.82\text{--}7.66$  (m, 2 H),  $7.58\text{--}7.40$  (m, 3 H),  $3.78\text{--}3.62$  (m, 1 H),  $3.60\text{--}3.33$  (m, 3 H),  $2.29\text{--}2.05$  (m, 2 H),  $1.64$  (d,  $^2J_{\text{H,P}} = 10.5$  Hz, 3 H),  $1.14$  (t,  $^3J_{\text{H,H}} = 7.0$  Hz, 3 H),  $0.75$  (qm,  $^1J_{\text{H,B}} = 92.9$  Hz, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 131.5$  (d,  $^2J_{\text{C,P}} = 9.4$  Hz),  $131.4$  (d,  $^4J_{\text{C,P}} = 2.5$  Hz),  $129.9$  (d,  $^1J_{\text{C,P}} = 54.7$  Hz),  $128.9$  (d,  $^3J_{\text{C,P}} = 10.1$  Hz),  $66.4$  (s),  $65.2$  (s),  $28.3$  (d,  $^1J_{\text{C,P}} = 35.9$  Hz),  $15.2$  (s),  $11.7$  (d,  $^1J_{\text{C,P}} = 38.4$  Hz).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.42$  (qm,  $^1J_{\text{P,B}} = 63.5$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{H}]^+$ : 209.1267; found: 209.1267.

#### tert-Butyl(2-ethoxy)ethylphenylphosphine-borane (12)

Prepared from phosphine-borane **9** (90  $\mu\text{L}$ , 0.5 mmol) and ethyl vinyl ether (58  $\mu\text{L}$ , 0.6 mmol); yield: 47%; translucent oil;  $R_f = 0.3$  ( $\text{CH}_2\text{Cl}_2$ ).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.80\text{--}7.67$  (m, 2 H),  $7.57\text{--}7.40$  (m, 3 H),  $3.82\text{--}3.68$  (m, 1 H),  $3.53\text{--}3.30$  (m, 1 H),  $3.43$  (t,  $^3J_{\text{H,H}} = 7.1$  Hz, 2 H),  $2.59\text{--}2.39$  (m, 1 H),  $2.32\text{--}2.14$  (m, 1 H),  $1.14$  (t,  $^3J_{\text{H,H}} = 7.1$  Hz, 3 H),  $1.11$  (d,  $^3J_{\text{H,P}} = 14.0$  Hz, 9 H),  $0.60$  (qm,  $^1J_{\text{H,B}} = 88.4$  Hz, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 133.4$  (d,  $^2J_{\text{C,P}} = 8.2$  Hz),  $131.4$  (d,  $^4J_{\text{C,P}} = 1.9$  Hz),  $128.5$  (d,  $^3J_{\text{C,P}} = 9.4$  Hz),  $125.9$  (d,  $^1J_{\text{C,P}} = 48.4$  Hz),  $66.4$  (s),  $65.5$  (d,  $^2J_{\text{C,P}} = 5.0$  Hz),  $29.2$  (d,  $^1J_{\text{C,P}} = 33.3$  Hz),  $25.4$  (d,  $^2J_{\text{C,P}} = 2.5$  Hz),  $19.9$  (d,  $^1J_{\text{C,P}} = 33.3$  Hz).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 27.82$  (qm,  $^1J_{\text{P,B}} = 69.7$  Hz).

#### Dicyclohexyl(2-butoxy)ethylphosphine-borane (13)

Prepared from phosphine-borane **10** (106 mg, 0.5 mmol), butyl vinyl ether (78  $\mu\text{L}$ , 0.6 mmol), and  $\text{Et}_3\text{B}$  (600  $\mu\text{L}$ , 1 mol·L $^{-1}$  in hexane); yield: 54%; translucent oil;  $R_f = 0.3$  (toluene).

$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta = 3.62$  (dt,  $^2J_{\text{H,P}} = 15.3$  Hz,  $^3J_{\text{H,H}} = 7.7$  Hz, 2 H),  $3.42$  (t,  $^3J_{\text{H,H}} = 6.5$  Hz, 2 H),  $2.00\text{--}1.68$  (m, 12 H),  $1.68\text{--}1.48$  (m, 4 H),  $1.48\text{--}1.10$  (m, 12 H),  $0.91$  (t,  $^3J_{\text{H,H}} = 7.3$  Hz, 3 H),  $1.00$  to  $-0.30$  (m, 3 H).

$^{13}\text{C}$  NMR (63 MHz,  $\text{CDCl}_3$ ):  $\delta = 70.8$  (s),  $65.9$  (d,  $^2J_{\text{C,P}} = 3.0$  Hz),  $31.9$  (d,  $^1J_{\text{C,P}} = 32.9$  Hz),  $31.8$  (s),  $27.0$  (d,  $^3J_{\text{C,P}} = 1.2$  Hz),  $26.9$  (s),  $26.8$  (d,  $^2J_{\text{C,P}} = 2.8$  Hz),  $26.7$  (d,  $^2J_{\text{C,P}} = 2.4$  Hz),  $26.0$  (d,  $^3J_{\text{C,P}} = 1.1$  Hz),  $19.8$  (d,  $^1J_{\text{C,P}} = 30.9$  Hz),  $19.4$  (s),  $13.9$  (s).

$^{31}\text{P}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.91$  (dm,  $^1J_{\text{P,B}} = 75.3$  Hz).

HRMS:  $m/z$  calcd for  $[\text{M} - \text{H}]^+$ : 311.2675; found: 311.2677.

**Dicyclohexyl(2-ethoxy)ethylphosphine-borane (14)**

Prepared from phosphine-borane **10** (106 mg, 0.5 mmol), ethyl vinyl ether (58  $\mu\text{L}$ , 0.6 mmol), and  $\text{Et}_3\text{B}$  (600  $\mu\text{L}$ , 1 mol-L<sup>-1</sup> in hexane); yield: 53%; translucent oil;  $R_f = 0.3$  (toluene).

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 3.63$  (dt, <sup>3</sup>J<sub>H,P</sub> = 15.5 Hz, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 2 H), 3.49 (q, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 2 H), 1.98–1.62 (m, 13 H), 1.48–1.13 (m, 11 H), 1.20 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 3 H), 0.25 (qm, <sup>1</sup>J<sub>H,B</sub> = 93.2 Hz, 3 H).

<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>):  $\delta = 66.2$  (s), 65.7 (d, <sup>2</sup>J<sub>C,P</sub> = 3.4 Hz), 31.9 (d, <sup>1</sup>J<sub>C,P</sub> = 32.9 Hz), 26.9 (d, <sup>3</sup>J<sub>C,P</sub> = 1.1 Hz), 26.8 (s), 26.7 (d, <sup>2</sup>J<sub>C,P</sub> = 2.5 Hz), 26.6 (d, <sup>2</sup>J<sub>C,P</sub> = 2.5 Hz), 25.9 (d, <sup>3</sup>J<sub>C,P</sub> = 1.2 Hz), 19.8 (d, <sup>1</sup>J<sub>C,P</sub> = 30.9 Hz), 15.2 (s).

<sup>31</sup>P NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 23.83$  (dm, <sup>1</sup>J<sub>P,B</sub> = 74.0 Hz).

HRMS: *m/z* calcd for [M – H]<sup>+</sup>: 283.2362; found: 283.2367.

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