# Synthesis and Reactions of {o-{[Bis(dimethylamino)boryl]methyl}phenyl}diphenylphosphane

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Dedicated to Professor Welf Bronger on the Occasion of his 65th Birthday

**Abstract.** The new  $\alpha\omega$ -[boryl(organyl)]phosphane o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>B(NMe<sub>2</sub>)<sub>2</sub> (**10**) was obtained in good yields from the reaction of ClB(NMe<sub>2</sub>)<sub>2</sub> with o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Li(tmeda). Five derivatives of **10** were obtained by substituting the boron-bound amino groups by reactions with MeOH, BCl<sub>3</sub>, HCl, and LiAlH<sub>4</sub>, respectively, in particular, o-Ph<sub>2</sub>(HCl)PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>BCl<sub>2</sub>(HNMe<sub>2</sub>) (**10 e**) which shows a unique P-H-Cl-H-N unit. Compound **10** and its derivatives were characterized by multinuclear NMR methods, mass spectra, and elemental analyses. In addition, the structure of  $10 e \cdot 1.5 C_6 H_6$  was determined by single crystal X-ray diffraction.

**Keywords:** (Borylorganyl)phosphanes; (Borylorganyl)phosphoniumsalt; X-ray structure

## Synthese und Reaktionen von {o-{[Bis(dimethylamino)boryl]methyl}phenyl}diphenyl-phosphan

Inhaltsübersicht. Das neue  $\alpha_{,\omega}$ -[Boryl(organyl)]phosphan o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>B(NMe<sub>2</sub>)<sub>2</sub> (10) wurde synthetisiert und spektroskopisch charakterisiert. Die Reaktivität dieser Verbindung, vor allem gegenüber Substitutionsreaktionen am Boratom war der Gegenstand unserer Untersuchungen. Verbindung 10 reagiert mit MeOH, BCl<sub>3</sub> bzw. HCl zu den Verbindungen o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>B(OMe)<sub>2</sub> (10 a),

 $o-Ph_2PC_6H_4CH_2BCl_2$  (10 c),  $o-Ph_2PC_6H_4CH_2BCl_2(HNMe_2)$ (10 d) und  $o-Ph_2P(HCl)C_6H_4CH_2BCl_2(HNMe_2)$  (10 e). Die Umsetzung von 10 a mit LiAlH<sub>4</sub> führt zu  $o-Ph_2PC_6H_4CH_2BH_2$  (10 b). Verbindung 10 e wurde zusätzlich durch eine Röntgenstrukturanalyse charakterisiert.

#### Introduction

The knowledge about  $\alpha,\omega$ -[boryl(organyl)]phosphanes of the type  $R_2P(CR'_x)_nBR''_2$  is restricted to few examples. Early investigations describe the syntheses and spectroscopic properties of compounds with a saturated organic bridge between phosphorus and boron such as  $Et_2P(CH_2)_2B[O_2(CH_2)_2]$  (1) [1] and the dimeric (Me\_2PCH\_2BMe\_2)\_2 (2) [2]. Recently we reported

Dr. Holger Braunschweig Institut für Anorganische Chemie der TH Templergraben 55 D-52056 Aachen about the synthesis of the first monomeric methylene bridged compound  $Me_2PCH_2B(NMe_2)_2$ (3) [3].  $Me_2P(CMe)_2BMe_2$  (4), the first example of an ethylene bridged compound was characterized in 1974 [4], and derivatives like  $E-Ph_2P(CH)_2BMes_2$  (Mes = 2,4,6- $Me_3C_6H_2$ ) (5) [5] were investigated with respect to their nonlinear optical properties. The attempted preparation of Mes<sub>2</sub>PBBr<sub>2</sub> from LiPMes<sub>2</sub> and BBr<sub>3</sub> leads to  $[2-(Br_2BCH_2)3,5-Me_2C_6H_2]Mes(H)P$  (6b) by 1,2addition of one CH moiety of an o-Me group to the phosphorus boron double bond in the intermediate (6a) [6]. This  $\alpha, \omega$ -[boryl(organyl)]phosphane exhibits an aromatic spacer between phosphorus and boron. A similar organic backbone, but now with phosphorus in benzyl position, is known from o-Ph<sub>2</sub>PCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>BtBu<sub>2</sub> (7) [7]. Characteristic for these compounds is the

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Fig. 1 (Borylorganyl)phosphanes

inter- or intramolecular formation of bonds between posphorus and the electron deficient boron. Exceptions, because of electronic or steric reasons, are compounds 1, 3, and 5, respectively.

So far, nothing about the reactivity of these compounds especially towards substitution reactions of the boron-bound groups, except of **3**, has been reported. As a phosphorus-bound ligand to various transition metal moieties such as  $[(CO)_4Fe]$ ,  $[(CO)_5Cr]$ , and  $[(MeCp)(CO)_2Mn]$  **3** undergoes substitution reactions at boron, while the corresponding reactions of the uncoordinated phosphane always lead to mixtures of compounds with tetracoordinated boron [3]. The reaction of  $[(CO)_4Fe\{Me_2PCH_2B(NMe_2)_2\}]$  **8** with MeOH gives the corresponding methoxyderivate  $[(CO)_4Fe\{Me_2PCH_2B(OMe)_2\}]$  **9** in good yields [3].

We have initiated systematic studies on compounds of the type  $R_2P(CR_m)_nBX_2$  (R = alkyl or aryl; m = 1, 2; n ≥ 1; X = H, NR<sub>2</sub>, OR, Hal) to investigate their properties as ligands in transition metal complexes. In particular, the formation of an intramolecular metal boron bond, which shall be favoured by chelating assistance, is the primary purpose of our work. Therefore it is necessary to gain information about the reactivity of the boryl moiety in  $\alpha,\omega$ -[Boryl (organyl)]phosphanes. This paper describes the synthesis and characterization of o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>B(NMe<sub>2</sub>)<sub>2</sub> (10) and its reactivity towards substitution reactions of the boron-bound amino groups.

#### **Results and Discussion**

#### Synthesis of 10

The phosphane **10** was obtained in good yields from the reaction of  $o-Ph_2PC_6H_4CH_2Li(tmeda)$  [8], with chloro[bis(dimethylamine)]borane [9]. The <sup>11</sup>B and <sup>31</sup>P NMR shifts of  $\delta = 33.85$  and -13.96 ppm, respectively, clearly demonstrate the absence of inter- or intramolecular boron phosphorus interactions.



#### Reactions of 10

We investigated exchange reactions at the B(NMe<sub>2</sub>)<sub>2</sub> moiety of **10** in order to generate a variety of potential bidentate ligands. The reaction of **10** (Eq. (2)) with MeOH gave the expected methoxy substituted derivative **10a**. Compound **10a** was isolated as a colourless solid showing in solution <sup>11</sup>B and <sup>31</sup>P NMR shifts at  $\delta = 30.72$  and -14.83 ppm, respectively, being in the expected range for threefold coordinated boron and phosphorus (Table 1). Addition of one equivalent of LiAlH<sub>4</sub> to **10a** led to the formation of the hydrogen substituted compound **10b**. Due to the absence of  $\pi$ -backbonding from hydrogen to boron coordination of phosphorus to boron occurs, leading to a highfield shifted <sup>11</sup>B NMR signal at  $\delta = -23.57$  and a downfield shifted <sup>31</sup>P NMR signal at  $\delta = 28.53$  (<sup>1</sup>J<sub>PB</sub> = 43 Hz).



By treatment of 10 with BCl<sub>3</sub> the expected chlorine compound 10 c was obtained as a white solid. Due to

compound	$\delta$ <sup>11</sup> B (ppm)	$\delta$ <sup>31</sup> P (ppm)
10	33.85	-13.96
10 a	30.72	-14.38
10 b	-23.57	28.53
10 c	6.51	-0.08
10 d	8.77	-12.58
10 e	8.41	-9.06

Table 1 <sup>11</sup>B and <sup>31</sup>P Data

a less effective  $\pi$ -backbonding from chlorine, the boron atom in **10 c** is more acidic and allows a coordination of the phosphorus atom which is proven by a highfield shifted <sup>11</sup>B NMR signal at  $\delta = 6.51$  and a lowfield shift of the phosphorus resonance at  $\delta =$ -0.08 ppm (<sup>1</sup>J<sub>PB</sub> = 105.60 Hz).

From the reactions of 10 with HCl we obtained two different products depending on the borane to HCl ratios (Eq. (3)). The addition of three equivalents HCl to a solution of 10 in toluene yielded the dimethylamine adduct 10d as a colourless solid. In this case, the coordination of the amine as the better donor is preferred to the formation of an intramolecular boron phosphorus bond as being indicated by a <sup>11</sup>B NMR shift of  $\delta = 8.77$  ppm for the fourfold-coordinated boron and a <sup>31</sup>P NMR signal at  $\delta = -12.58$  ppm. A bridging position of the ammonium proton between nitrogen and phosphorus can be excluded from the absence of a coupling to phosphorus for this proton. Addition of four equivalents HCl to 10 led to the formation of the phosphonium salt 10 e. The two hydrogen atoms being coordinated to the phosphonium and ammonium moieties, respectively, show low field shifted signals at 9.42 and 11.32 ppm, the latter exhibiting a  ${}^{1}J_{PH}$  coupling of 540 Hz.



In the crystal 10e adopts a geometry consisting of a nine membered ring, which is fused with the aromatic ligand between phosphorus and boron. The larger ring

contains a P-H-Cl-H-N unit with a bridging hydrogen atom between each phosphorus and nitrogen on the one side and chlorine on the other side. Boron, nitrogen, and phosphorus show each a distorted tetrahedal coordination with interatomic angles between  $101.6(9)^{\circ}$ and  $116(1)^{\circ}$  (table 2). The chloride anion is bonded to the cation by two hydrogen bridges; the N-H and P-H distances are marked by usually observed high standard deviations and are shortened [10]. The geometries of the two bridging units, however, are consistent with literature data. Both hydrogen bridges are almost linear (angles P-H…Cl =  $162(2)^{\circ}$  and N-H…Cl =  $168(2)^{\circ}$ ), and include an angle of  $86.3(8)^{\circ}$  at the chloride ion.

1095

**Table 2** Selected Bond Distances (Å) and Angles (deg) for10 e

distances (Å	r) 	angles (deg)	
<b>P</b> –H1	1.28(2)	C10PH1	116(1)
Cl3-H1	2.44(2)	Cl3-H1-P	162(1)
Cl3–H2	2.22(2)	H1-Cl3-H2	86.3(8)
N-H2	0.92(2)	Cl3-H2-N	168(2)
N–B	1.595(2)	H2–N–B	105(1)
C1–B	1.611(3)	N-BC1	110.4(1)
C1–C11	1.499(2)	C11–C1–B	115.8(1)
C10-C11	1.397(2)	C1-C11-C10	123.7(2)
<b>PC10</b>	1.795(2)	C11-C10-P	122.1(1)
P-C20	1.794(2)	C20-P-C30	109.90(9)
P-C30	1.788(2)	C2-N-C3	109.0(2)
Cl1–B	1.885(2)	Cl1-B-Cl2	108.4(1)
Cl2-B	1.859(2)	C30-P-H1	101.6(9)



Fig. 2 Platon plot of 10 e; ellipsoids with 30% probability

Stelzer et al. [11] and Bricklebank et al. [12] reported about P-H...Br bridges. The H...Cl distance of 2.21(3) Å of the hydrogen bridge between nitrogen and chloride is comparable to the situation found in the compound  $[NH(CH_3)_3]_2[ZnCl_4]$  [13]. To our knowledge the phosphonium salt **10 e** is the first fully characterized compound of this type.

### Conclusions

The new  $\alpha\omega$ -[boryl(organyl)]phosphane 10 exhibits a variety of exchange reactions yielding several boron substituted derivatives. Exchange of the dimethylamino groups of 10 by treatment with MeOH and BCl<sub>3</sub> proceeded in the expected way forming the dimethoxy- (10 a) and dichloroborane (10 c), respectively, indicating no exceptional behaviour. Reaction of 10 a with LiAlH<sub>4</sub> led to the dihydroborane 10 b. Two different products can be isolated by reaction of 10 with HCl, depending on the borane to HCl ratios. The dimethylamine adduct 10 d was obtained by treatment of 10 with three equiv. of HCl, whereas the phosphonium salt 10 e was formed by the reaction of 10 with four equiv. of HCl.

In order to achieve our purpose, the formation of a metal boron bond by chelate assistance, it is now necessary to introduce the compounds **10 a-e** to a variety of metal complexes. Detailed studies on the chemical behaviour of the new ligands **10 a-e** towards transition metal complexes will be subject of a following paper.

#### **Experimental Section**

**General Considerations.** All manipulations were carried out by standard Schlenk techniques under N<sub>2</sub>. All reagents were purchased from commercial suppliers and used without further purification. Solvents and deuterated solvents for NMR experiments were dried and purified by standard methods. o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Li(tmeda) [8] and ClB(NMe<sub>2</sub>)<sub>2</sub> [9] were prepared similar to literature procedures.

**Spectroscopic Studies.** <sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, and <sup>31</sup>P NMR data were obtained on a Varian Unity 500 in CDCl<sub>3</sub> as solvent with TMS as internal,  $BF_3 \cdot OEt_2$ , and  $H_3PO_4$  (85%) as external standards. IR spectra were recorded on a Perkin-Elmer FT-IR 1720 X spectrometer in CHCl<sub>3</sub> solutions. Mass spectra were recorded on a Finnigan MAT 95 (70 eV) and elemental analyses (C, H, N) were obtained from a Carlo-Erba elemental analyser, Modell 1106.

Synthesis of  $o-Ph_2PC_6H_4CH_2B(NMe_2)_2$  (10). 1.75 g (13.06 mmol) (Me<sub>2</sub>N)<sub>2</sub>BCl in 50 mL hexane were added to 5.20 g (13.06 mmol)  $o-Ph_2PC_6H_4CH_2Li(\text{tmeda})$  in 70 mL thf at -78 °C. The reaction mixture was warmed up to room temperature and all volatiles were removed under high vacuum. The residue was extracted with 150 mL hexane and filtered. The pure compound was obtained as a white solid from the filtrate at -30 °C. Yield: 3.36 g, 68.9%. <sup>1</sup>H NMR:  $\delta = 2.51$  (s, 12 H, NCH<sub>3</sub>), 2.67 (s, 2 H, CH<sub>2</sub>B), 6.92–7.42 (m, 14 H PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR:  $\delta = 33.85$ . <sup>13</sup>C NMR:  $\delta = 23.20$  (br,

CH<sub>2</sub>B), 40.40 (s, NCH<sub>3</sub>) 125.19–147.37 (PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P NMR:  $\delta = -13.96$ . MS *m/z* (intensity %, fragment) = 328 (7%, M<sup>+</sup>–NMe<sub>2</sub>), 275 (100%, M<sup>+</sup>–B(NMe<sub>2</sub>)<sub>2</sub>), 197 (22%, M<sup>+</sup>–B(NMe<sub>2</sub>)<sub>2</sub>–C<sub>6</sub>H<sub>5</sub>), 183 (30%, M<sup>+</sup>–B(NMe<sub>2</sub>)<sub>2</sub>–C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), 55 (10%, BNMe<sub>2</sub>). Anal. C<sub>23</sub>H<sub>28</sub>BN<sub>2</sub>P (374.30): C, 74.43 (73.81 calc.); H, 7.76 (7.54); N, 7.02 (7.48).

**Synthesis of** *o*-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>B(OMe)<sub>2</sub> (10 a). 2.52 g (6.74 mmol) 10 in 30 mL toluene were reacted with two equivalents of methanol at 0 °C. The reaction mixture was warmed up to room temperature and concentrated to 15 mL. The pure compound was obtained as a white solid at -30 °C. Yield: 2.13 g, 90.1%. <sup>1</sup>H NMR:  $\delta = 2.51$  (d, <sup>4</sup>J<sub>PH</sub> = 2.75 Hz, 2 H, CH<sub>2</sub>B), 3.32 (s, 6 H, BOCH<sub>3</sub>), 6.90–7.42 (m, 14 H PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR:  $\delta = 30.72$ . <sup>13</sup>C NMR:  $\delta = 23.20$  (br, CH<sub>2</sub>B), 49.99 (s, OCH<sub>3</sub>) 124.33–144.79 (PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P NMR:  $\delta = -14.38$ . MS *m*/*z* (intensity %, fragment) = 348 (10%, M<sup>+</sup>), 333 (1%, M<sup>+</sup>–Me), 316 (5%, M<sup>+</sup>–OMe), 275 (5%, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), 183 (1%, P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>), 72 (100%, B(OMe)<sub>2</sub>). Anal. C<sub>21</sub>H<sub>22</sub>BO<sub>2</sub>P (348.20): C, 73.13 (72.44 calc.); H, 6.76 (6.37).

Synthesis of o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>BH<sub>2</sub> (10b). A suspension of 0.24 g (6.40 mmol) LiAlH<sub>4</sub> in 20 mL Et<sub>2</sub>O was added dropwise to a vigorously stirred solution of 2.22 g (6.40 mmol) {2-[(dimethoxyboryl)methyl]phenyl}di-phenyl-phosphane in 50 mL Et<sub>2</sub>O at -78 °C. The reaction mixture was warmed up to room temperature and filtered. Residual dissolved aluminium salts were destroyed by addition of io-dine. The solvent was removed in high vacuum. The residue was condensed into a precooled flask at  $10^{-4}$  mbar and 125 °C. Recrystallisation from toluene yielded 1.15 g (62.5%) o-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>BH<sub>2</sub> (10 b).

<sup>1</sup>H NMR = 2.82 (d, tr, <sup>3</sup>J<sub>PH</sub> = 18.62 Hz, <sup>3</sup>J<sub>HH</sub> = 4.88 Hz, 2 H, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>BH<sub>2</sub>P), 2.40–3.20 (m, br, CH<sub>2</sub>BH<sub>2</sub>P), 6.89–7.58 (m, 14 H, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) ppm; <sup>1</sup>H{<sup>11</sup>B} NMR  $\delta$  = 2.82 (d, <sup>2</sup>J<sub>PH</sub> = 3.66 Hz, CH<sub>2</sub>BH<sub>2</sub>P), u.a. ppm; <sup>11</sup>B NMR  $\delta$  = -23.57 (d, tr, <sup>1</sup>J<sub>PB</sub> = 43 Hz, <sup>1</sup>J<sub>BH</sub> = 103.77 Hz) ppm; <sup>13</sup>C NMR  $\delta$  = 25.00 (s, br, PCH<sub>2</sub>B), 125.78–159.71 (m, o-, m-, p-, ipso-C, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>) ppm; <sup>31</sup>P{<sup>1</sup>H} NMR  $\delta$  = 28.53 (d, <sup>1</sup>J<sub>PB</sub> = 43 Hz) ppm; MS: *m*/z (intensity %, fragment) = 286 (100%, M<sup>+</sup>-2 H), 275 (1%, M<sup>+</sup>-BH<sub>2</sub>), 91 (5%, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>+</sup>); Anal. C<sub>19</sub>H<sub>18</sub>BP (288.16): C, 78.87 (79.19 calc.); H, 6.28 (6.30).

**Synthesis of** *o***-Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>BCl<sub>2</sub> (10 c).** 3.21 g (8.58 mmol) **10** in 50 mL toluene were reacted with 14.03 mL of a 0.613 M solution of BCl<sub>3</sub> in toluene at 0 °C. The reaction mixture was warmed up to room temperature within 1 h, filtered and concentrated to 25 mL. The pure compound was obtained as a colourless solid at -30 °. Yield: 2.59 g, 85.2%. <sup>1</sup>H NMR  $\delta$  = 2.51 (d, <sup>3</sup>J<sub>PH</sub> = 13.74 Hz, 2 H, CH<sub>2</sub>B), 7.25-7.68 (m, 14 H PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>11</sup>B NMR:  $\delta$  = 6.51. <sup>13</sup>C NMR:  $\delta$  = 36.66 (br, CH<sub>2</sub>B), 126.86–153.62 (PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P NMR:  $\delta$  = -0.08 (q, br, <sup>1</sup>J<sub>PB</sub> = 105.60 Hz). MS *m/z* (intensity %, fragment) = 356 (1%, M<sup>+</sup>), 320 (1%, M<sup>+</sup>-Cl), 275 (5%, M<sup>+</sup>-BCl<sub>2</sub>), 261 (1%, M<sup>+</sup>-CH<sub>2</sub>BCl<sub>2</sub>), 91 (100%, C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>). Anal. Calcd. for C<sub>19</sub>H<sub>16</sub>BCl<sub>2</sub>P (357.05): C, 63.47 (63.92 calc.); H, 5.00 (4.52).

Synthesis of  $o-Ph_2PC_6H_4CH_2BCl_2(HNMe_2)$  (10 d). 5.20 mL of a 3 M solution of HCl in Et<sub>2</sub>O were added dropwise to 1.95 g (5.20 mmol) 10 in 40 mL toluene at -78 °C. The reaction mixture was warmed up to room temperature, filtered

and concentrated to 20 mL. The pure compound was obtained as a white solid by crystallization from benzene. Yield: 1.62 g, 77.5%. <sup>1</sup>H NMR: = 2.39 (s, 6H, NCH<sub>3</sub>), 2.85 (s, 2 H, CH<sub>2</sub>B), 6.65–7.80 (m, 14 H PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>), 10.05 (s, 1 H, NH). <sup>11</sup>B NMR:  $\delta = 8.77$ . <sup>13</sup>C NMR:  $\delta = 33.34$  (br, CH<sub>2</sub>B), 37.78 (s, NCH<sub>3</sub>), 125.33–150.60 (PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P NMR:  $\delta = -12.58$ . Anal. C<sub>21</sub>H<sub>23</sub>BCl<sub>2</sub>NP (402.13): C, 63.25 (62.73 calc.); H, 5.21 (5.76); N, 3.56 (3.48).

**Synthesis of** *o*-Ph<sub>2</sub>(HCl)PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>BCl<sub>2</sub>(HNMe<sub>2</sub>) (10 e). 19 mL of a 0.48 M solution of HCl in Et<sub>2</sub>O were added dropwise to 0.85 g (2.30 mmol) **10** in 40 mL toluene at -78 °C. The reaction mixture was warmed up to room temperature, filtered and concentrated to 20 mL. The pure compound was obtained as colourless crystals from benzene. Yield: 0.70 g, (69.4%). <sup>1</sup>H NMR:  $\delta = 2.68$  (s, 2 H, CH<sub>2</sub>B), 2.71 (d, <sup>3</sup>J<sub>HH</sub> = 4.26 Hz, 6 H, NCH<sub>3</sub>), 7.20–7.90 (m, 14 H PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>), 9.42 (br, 1 H, NH), 11.32 (d, <sup>1</sup>J<sub>PH</sub> = 540 Hz, 1 H, PH). <sup>11</sup>B NMR:  $\delta = 8.41$ . <sup>13</sup>C NMR:  $\delta = 32.16$  (br, CH<sub>2</sub>B), 37.64 (s, NCH<sub>3</sub>), 125.18–150.00 (PC<sub>6</sub>H<sub>5</sub> and PC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P NMR:  $\delta = -9.06$ . MS *m*/*z* (intensity %, fragment) = 365 (30%, M<sup>+</sup>-HCl-Cl), 330 (18%, M<sup>+</sup>-HCl-2 Cl), 320 (100%, M<sup>+</sup>-HCl-Cl-HNMe<sub>2</sub>), 275 (5%, Ph<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>), 196 (18%, M<sup>+</sup>-HCl-HNMe<sub>2</sub>-BCl<sub>2</sub>-Ph). Anal. C<sub>21</sub>H<sub>24</sub>BCl<sub>3</sub>NP (438.59): C, 56.87 (57.51 calc.); H, 5.11 (5.52); N, 3.82 (3.19).

Structure Determination of 10 e. The compound crystallizes in the triclinic space group  $P\overline{1}$  with 1.5 mol benzene *per* mol

**Table 3** Summary of X-ray Crystallographic Data for  $10 e \cdot 1.5 C_6 H_6$ 

_	
empirical formula	C <sub>30</sub> H <sub>33</sub> BCl <sub>3</sub> NP
a, Ā	9.9071(9)
b, Å	12.966(1)
<i>c</i> , Å	13.138(1)
$\alpha$ , deg	112.745(6)
$\beta$ , deg	98.793(7)
$\lambda$ , deg	97.315(7)
V, Å <sup>3</sup>	1505.7(3)
Ź	2
fw	555.75
cryst syst	triclinic
space group	<i>P</i> 1 (No 2)
diffractometer	Enraf Nonius CAD4
temp, °C	20
γ, Å	1.54184
$\rho_{\rm calc.}, {\rm g \ cm^{-3}}$	1.226
$\mu,  \mathrm{cm}^{-1}$	34.55
no. of observations	4998 $I > 1\sigma(I)$
no. of variables	433
R	0.048
R <sub>w</sub>	0.066
$w^{-1} = \sigma_{(Fo)}^2$	

borylphosphane, *i. e.* one benzene in general position and the other located around an inversion center. Geometry and intensity data were collected on an ENRAF Nonius CAD4 diffractometer equipped with a graphite monochromator. A summary of crystallographic data, data collection parameters, and convergence results is given in Table 3. The structure was solved by direct methods [14]. After completion of the isotropic structure model, all hydrogen atoms could be located in Fourier difference syntheses. In the final full-matrix refinement, non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the benzene molecule in general position were treated as riding atoms (C-H = 0.98 Å,  $U_{\rm H} = 1.3$   $U_{\rm C}$ ) and the remaining H atoms were refined isotropically [15].

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