

1-*tert*-Butyl-2-methylphospholane–borane and its coupling product 2,2′-bis(1-*tert*-butylphospholane–borane)

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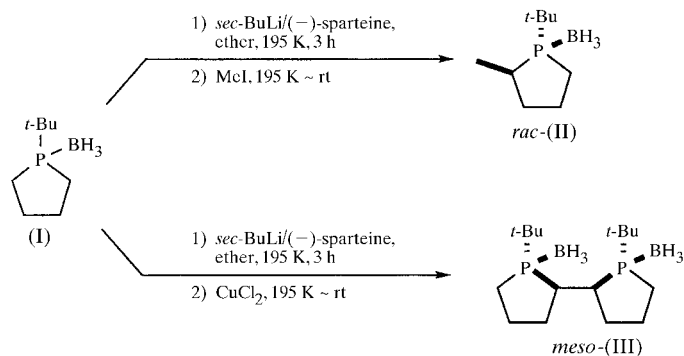
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The title compound, $C_9H_{22}BP$, and its coupling product, $C_{16}H_{38}B_2P_2$, were synthesized and their crystal structures analyzed by X-ray diffraction. The molecular structures clearly explain the stereoselective reaction pathways leading to the products. The average P–B distance and C–P–B angle are 1.929 Å and 114°, respectively.

Comment

Optically active phosphines have played an important role as chiral ligands in various metal-catalyzed asymmetric reactions. Among them, trialkylphosphines are known to be highly reactive due to donating lone-pair electrons on the P atom. In our previous work (Imamoto *et al.*, 1998), P-chirogenic bistralkylphosphine ligands, (*S,S*)-1,2-bis[boranato(alkyl)-methylphosphino]ethanes (alkyl = *tert*-butyl, 1,1-diethylpropyl, 1-adamantyl, cyclopentyl or cyclohexyl), are extremely effective in the asymmetric hydrogenation of various α,β -unsaturated α -amino acids and their esters. In order to obtain more effective asymmetric reactions, we intended to design and synthesize further trialkylphosphine ligands with a more rigid structure.



1-*tert*-Butylphospholane–borane, (I), was synthesized from phosphorus trichloride and 1,4-butanebis(magnesium bromide). The enantioselective deprotonation of (I) was performed using *sec*-butyllithium and (–)-sparteine as a chiral

source (Muci *et al.*, 1995). The monophosphine–borane, (*rac*)-1-*tert*-butyl-2-methylphospholane–borane, (II), was synthesized in almost 100% yield by deprotonation of (I) and the subsequent reaction with methyl iodide. Although a (–)-sparteine/*sec*-butyllithium reagent system was used, racemic (II) was obtained.

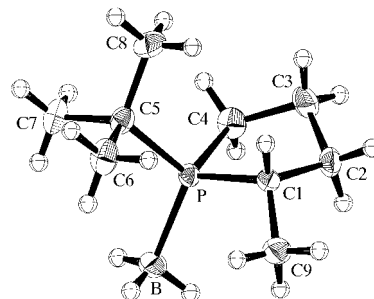


Figure 1
ORTEP (Johnson, 1976) drawing of (II).

The ORTEP (Johnson, 1976) drawing of the molecular structure of (II) is shown in Fig. 1. The conformation around the P–C1 bond is an almost eclipsed form; the torsion angles of B–P–C1–C9 and C4–P–C1–C2 are $-25.4(3)$ and $-18.1(2)^\circ$, respectively. This conformation suggests that the methyl group should attack the generated anionic C1 atom from the less sterically hindered side to avoid the heavy steric repulsion with the bulky *tert*-butyl group. This may indicate that (II) was produced in a perfect diastereoselective way. The oxidative coupling reaction of (I) was performed using cupric chloride instead of methyl iodide after deprotonation of (I). *meso*-2,2′-Bis(1-*tert*-butylphospholane–borane), (III), was obtained in *ca* 10% yield, with 40% recovery of the starting material.

The ORTEP (Johnson, 1976) drawing of the molecular structure of (III) is shown in Fig. 2. It clearly indicates that the molecule is a *meso* structure. The formation of this *meso* compound rather than its racemic form can be explained by considering the steric repulsion of the two *tert*-butyl groups. Thus, two generated radicals approach from the most sterically favorable side. The heavy steric repulsion may cause the low reaction yield of (III).

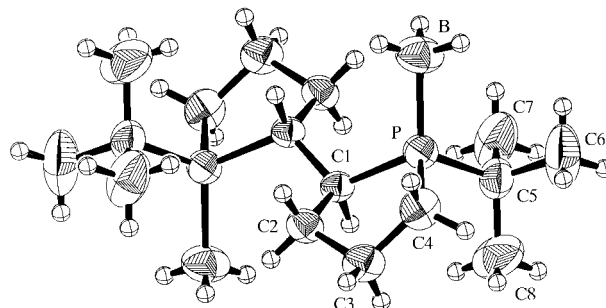


Figure 2
ORTEP (Johnson, 1976) drawing of (III).

Selected bond distances, angles, and torsion angles are listed in Tables 1 and 2. The corresponding distances and angles are in good agreement between the two molecules. The average P—B distance and C—P—B angle are 1.929 Å and 114°, respectively. There are no short contacts between the molecules in the two crystal structures.

Experimental

To a solution of *sec*-butyllithium and (–)-sparteine in ether was added (I) at 195 K. After the mixture was stirred for 3 h, methyl iodide or cupric chloride was added. Both crude products were purified by column chromatography on silica gel using toluene/hexane (20:1) as the eluent. Compound (II) was obtained as colorless cubes on standing under reduced pressure. Compound (III) was recrystallized from chloroform.

Compound (II)

Crystal data

C₉H₂₂BP
M_r = 172.06
 Orthorhombic, *Pna*2₁
a = 12.52 (2) Å
b = 6.944 (1) Å
c = 12.919 (1) Å
V = 1123 (1) Å³
Z = 4
D_x = 1.017 Mg m⁻³

Cu *Kα* radiation
 Cell parameters from 25 reflections
 $\theta = 7.3\text{--}34.7^\circ$
 $\mu = 1.690\text{ mm}^{-1}$
T = 123.2 K
 Prismatic, colorless
 0.40 × 0.30 × 0.30 mm

Data collection

Rigaku AFC-7S diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.576$, $T_{\max} = 0.602$
 1056 measured reflections
 1056 independent reflections
 1030 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.02$
 $\theta_{\text{max}} = 67.61^\circ$
 $h = -15 \rightarrow 0$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 15$
 3 standard reflections every 150 reflections intensity decay: 1%

Refinement

Refinement on *F*
R = 0.039
wR = 0.050
S = 1.913
 1030 reflections
 102 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.012$
 $\Delta\rho_{\text{max}} = 0.40\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34\text{ e \AA}^{-3}$
 Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
 Extinction coefficient: 0.035 (7)

Table 1

Selected geometric parameters (Å, °) for (II).

P—C1	1.843 (4)	P—B	1.926 (4)
P—C4	1.829 (4)	C1—C9	1.523 (4)
P—C5	1.851 (4)		
C1—P—C4	95.7 (2)	C4—P—C5	109.8 (2)
C1—P—C5	107.8 (2)	C4—P—B	112.0 (2)
C1—P—B	116.2 (2)	C5—P—B	113.9 (2)
C2—C1—P—C4	-18.2 (2)	C9—C1—P—B	-25.1 (4)
C5—P—C1—C9	104.1 (3)		

Compound (III)

Crystal data

C₁₆H₃₈B₂P₂
M_r = 314.04
 Monoclinic, *C2/c*
a = 10.346 (1) Å
b = 9.796 (2) Å
c = 20.597 (1) Å
 $\beta = 100.805 (8)^\circ$
V = 2050.5 (4) Å³
Z = 4

D_x = 1.017 Mg m⁻³
 Cu *Kα* radiation
 Cell parameters from 20 reflections
 $\theta = 22.1\text{--}24.7^\circ$
 $\mu = 1.817\text{ mm}^{-1}$
T = 296.2 K
 Prismatic, colorless
 0.48 × 0.30 × 0.20 mm

Data collection

Rigaku AFC-5S diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.517$, $T_{\max} = 0.695$
 1945 measured reflections
 1839 independent reflections
 1376 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 67.57^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 11$
 $l = -24 \rightarrow 24$
 3 standard reflections every 150 reflections intensity decay: 0.76%

Refinement

Refinement on *F*
R = 0.048
wR = 0.058
S = 1.787
 1423 reflections
 92 parameters
 H-atom parameters not refined

$w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.010$
 $\Delta\rho_{\text{max}} = 0.23\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18\text{ e \AA}^{-3}$
 Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
 Extinction coefficient: 0.086 (5)

Table 2

Selected geometric parameters (Å, °) for (III).

P—C1	1.859 (3)	P—B	1.919 (4)
P—C4	1.834 (3)	C1—C1 ⁱ	1.534 (4)
P—C5	1.854 (3)		
C1—P—C4	95.1 (1)	C4—P—C5	107.2 (1)
C1—P—C5	110.7 (1)	C4—P—B	110.5 (2)
C1—P—B	115.8 (2)	C5—P—B	115.4 (2)
C1—C1 ⁱ —P ⁱ —C5 ⁱ	109.7 (3)	C2—C1—P—C4	15.6 (2)
C1—C1 ⁱ —P ⁱ —B ⁱ	-24.1 (3)		

Symmetry code: (i) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$.

No Friedel reflections were measured for (I) and consequently we were unable to determine the correct direction of the polar axis in this system.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1100). Services for accessing these data are described at the back of the journal.

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