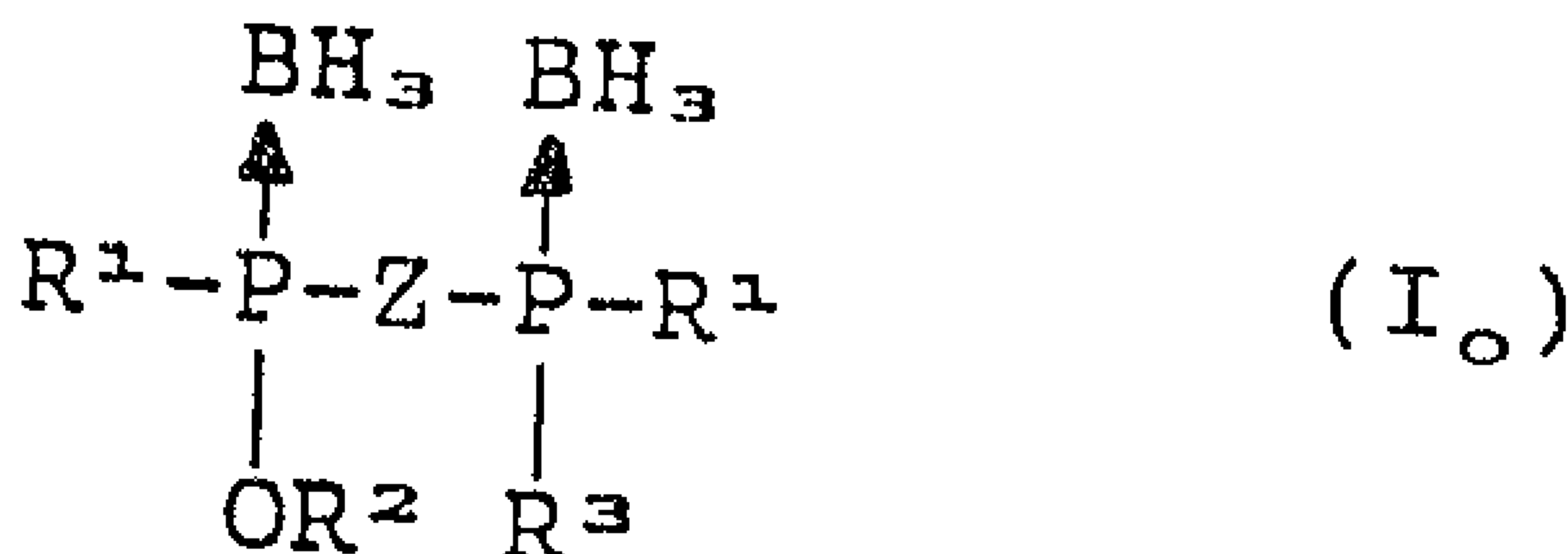




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(54) Title: CHIRAL PHOSPHINITE-BORANES AND THEIR PREPARATION AND USE



(57) **Abrégé/Abstract:**

The present invention relates, by way of novel industrial products, to the phosphinite-borane compounds of the general formula (see formula I_o) in which R¹ and R², which are identical or different, are each a C₁-C₁₈-alkyl group, a C₅-C₁₈-cycloalkyl group, a C₇-C₁₈-aralkyl group or a C₆-C₁₄-aryl group, it being possible for each of these groups to carry functional groups, R³ is a C₁-C₁₈-alkyl, C₅-C₁₈-cycloalkyl, C₇-C₁₈-aralkyl, C₆-C₁₄-aryl, C₁-C₁₈-alkoxy, C₇-C₁₈-cyclo-alkoxy, C₇-C₁₈-aralkoxy or C₆-C₁₄-aryloxy group, and Z is a bridge linking the two phosphorus atoms, said bridge being (i) a hydrocarbon chain having from 1 to 12 catenary C atoms, or (ii) a heterohydrocarbon chain containing from 2 to 12 catenary C atoms and at least one catenary heteroatom selected from O, S, Si, P and N, with the further condition that (i) Z is other than CH₂ when R¹ = phenyl and R² = R³ = methyl simultaneously, and (ii) Z is other than CH₂CH₂ when R¹ = phenyl, R² = methyl and R³ = methoxy simultaneously. These products are useful in the synthesis of chiral diphosphine compounds.



ABSTRACT OF THE DISCLOSURE

The present invention relates, by way of novel industrial products, to the phosphinite-borane compounds of the general formula



in which

R^1 and R^2 , which are identical or different, are each a C_1 - C_{18} -alkyl group, a C_5 - C_{18} -cycloalkyl group, a C_7 - C_{18} -aralkyl group or a C_6 - C_{14} -aryl group, it being possible for each of these groups to carry functional groups,

R^3 is a C_1 - C_{18} -alkyl, C_5 - C_{18} -cycloalkyl, C_7 - C_{18} -aralkyl, C_6 - C_{14} -aryl, C_1 - C_{18} -alkoxy, C_7 - C_{18} -cycloalkoxy, C_7 - C_{18} -aralkoxy or C_6 - C_{14} -aryloxy group, and

Z is a bridge linking the two phosphorus atoms, said bridge being (i) a hydrocarbon chain having from 1 to 12 catenary C atoms, or (ii) a heterohydrocarbon chain containing from 1 to 12 catenary C atoms and at least one catenary heteroatom selected from O, S, Si, P and N,

with the further condition that (i) Z is other than CH_2 when R^1 = phenyl and R^2 = R^3 = methyl simultaneously, and (ii) Z is other than CH_2CH_2 when R^1 = phenyl, R^2 = methyl and R^3 = methoxy simultaneously.

These products are useful in the synthesis of chiral diphosphine compounds.

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CHIRAL PHOSPHINITE-BORANES AND THEIR PREPARATION
AND USE

10

FIELD OF THE INVENTION

The present invention relates to a novel class of phosphinite compounds, especially chiral phosphinite
15 compounds. It relates more precisely to the phosphi-
nite-borane compounds of formula I₀ below, in which the
two phosphorus atoms are both complexed by (or bonded
to) a borane group. These phosphinite-borane compounds
carry one or more labile or substitutable groups per-
20 mitting nucleophilic substitution, for example by an
alkylating, cycloalkylating or arylating group.

The present invention further relates to the
methods of preparing these phosphinite-borane compounds
and to their uses in the preparation of diphosphines.

25

PRIOR ART

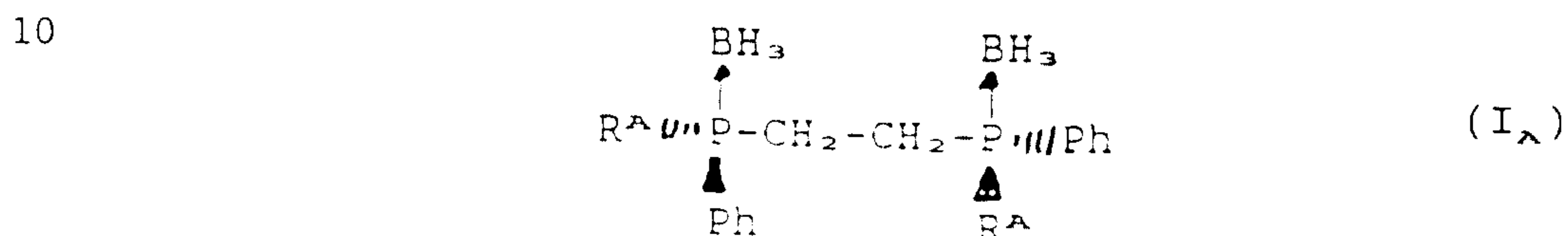
It is known that phosphinite compounds, and
particularly those which are optically active, are
industrially useful both *per se* and as starting mate-
30 rials for the preparation of other useful chiral
products such as, in particular, phosphine oxides,
phosphines, etc.

Numerous natural and synthetic products can now
be prepared by asymmetric synthesis catalyzed by means
35 of transition metals, and especially with catalysts

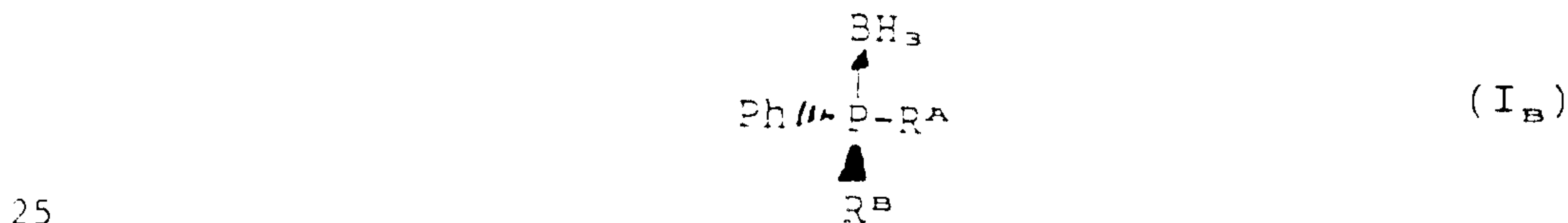
- 2 -

containing optically active organophosphorus ligands. The asymmetric synthesis route makes it possible to obtain substances which are of value in the fields of agriculture, food, pharmacy or perfumery. Known
 05 examples illustrating said asymmetric synthesis route are the production of L-dopa, L-phenylalanine, menthol or citronellol.

The preparation of two compounds of the formula



15 in which R^A is ortho-anisyl or 2-naphthyl, is known from an article by the co-inventors of the present invention, namely S. JUGE et al., Tetrahedron Letters 31 (no. 44) pages 6357-6360 (1990). The two compounds of formula I_A according to scheme 2 in said article
 20 (see page 6358) are obtained from



(in which R^A is defined as indicated above and R^B is CH_3) by the reaction of two mol of I_B with (i) s-BuLi, then (ii) CuCl_2 .

30 Said article, also describes

(a) the preparation of the starting compounds of formula I_B , and

35 (b) the preparation of chiral 1,2-diphosphinoethane complexes of the formula I_A .

-3-

In another connection, two products of formula I_o , namely the compound in which $R^1 = \text{Ph}$, $R^2 = \text{Me}$, $R^3 = \text{Me}$ and $Z = \text{CH}_2$ and, respectively, the compound in which $R^1 = \text{Ph}$, $R^2 = \text{Me}$, $R^3 = \text{MeO}$ and $Z = \text{CH}_2\text{CH}_2$, are known from Examples 21 and 22 of published PCT international patent application WO 91/00286 (publication date: 10th January 1991).

SUBJECT OF THE INVENTION

According to a first feature of the invention, a novel phosphinite compound substituted by BH_3 on the phosphorus is provided which is selected from the group consisting of the phosphinite-borane products of the general formula



in which

R^1 and R^2 , which are identical or different, are each a C_1 - C_{18} -alkyl group, a C_5 - C_{18} -cycloalkyl group, a C_7 - C_{18} -aralkyl group or a C_6 - C_{14} -aryl group,

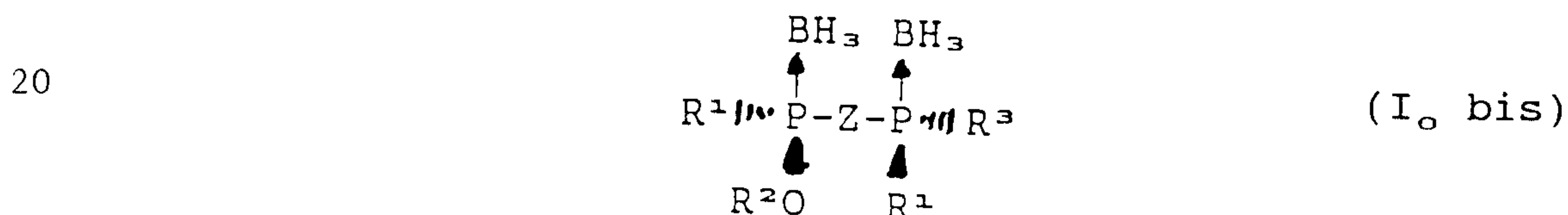
it being possible for each of these groups to carry functional groups,

05 R^3 is a C_1 - C_{18} -alkyl, C_5 - C_{18} -cycloalkyl, C_7 - C_{18} -aralkyl, C_6 - C_{14} -aryl, C_1 - C_{18} -alkoxy, C_7 - C_{18} -cycloalkoxy, C_7 - C_{18} -aralkoxy or C_6 - C_{14} -aryloxy group, and

10 Z is a bridge linking the two phosphorus atoms, said bridge being (i) a hydrocarbon chain having from 1 to 12 catenary C atoms, or (ii) a heterohydrocarbon chain containing from 1 to 12 catenary C atoms and at least one catenary heteroatom selected from O, S, Si, P and N,

15 with the further condition that (i) Z is other than CH_2 when R^1 = phenyl and R^2 = R^3 = methyl simultaneously, and (ii) Z is other than CH_2CH_2 when R^1 = phenyl, R^2 = methyl and R^3 = methoxy simultaneously.

From a chiral point of view, a compound of formula I_o can be represented by the following structure:



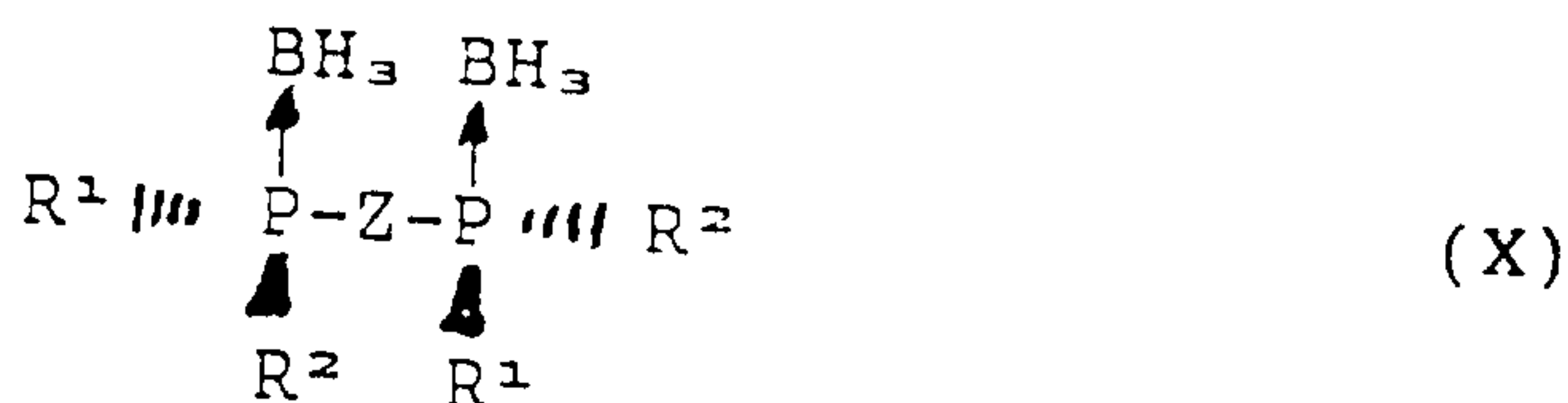
where R^1 , R^2 , R^3 and Z are defined as indicated above.

25 According to a second feature of the invention, a general method of preparing a phosphinite-borane compound of formula I_o or I_o bis is provided, said method comprising the reaction of an organometallic compound derived from a phosphinite-borane with a non-organometallic phosphinite-borane compound. Said organometallic compound is preferably an organolithium compound.

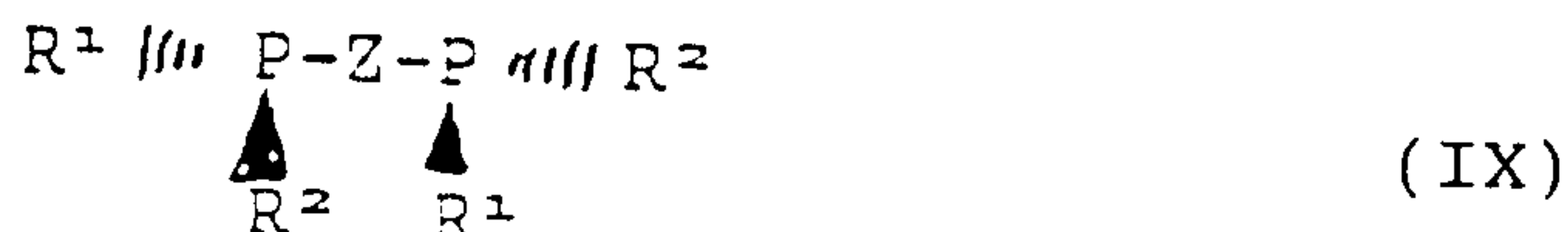
30 According to a third feature of the invention, the use of said phosphinite-borane compounds of formula I_o or I_o bis is provided for the preparation of other

chiral compounds, especially the diphosphine-diborane products of formula X and the diphosphine products of formula IX:

05



10 or



15 where R^1 , R^2 and Z are defined as indicated above.

More precisely, the phosphinite-borane compounds according to the invention are, in particular, converted to diphosphine-diborane compounds which are of high diastereoisomeric purity or essentially diastereoisomerically pure. These diphosphine-diborane compounds are then easily decomplexed (decomplexation is understood here as meaning the removal of the two borane groups, BH_3) at 50°C by means of a secondary amine such as diethylamine.

25

ABBREVIATIONS

For the sake of convenience, the following abbreviations have been used in the present description:

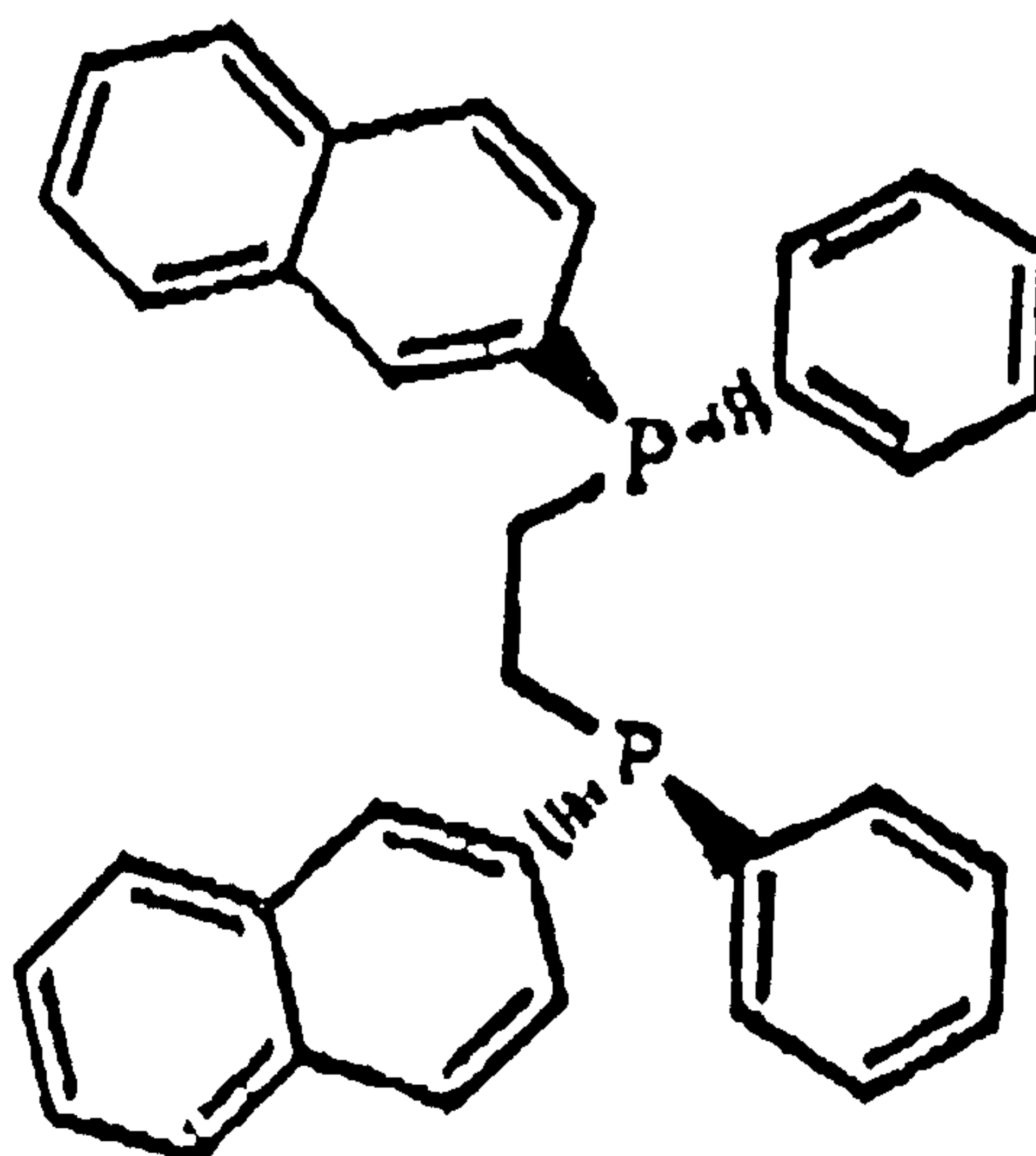
30 bNp = beta-naphthyl (i.e. 2-naphthyl)
BNPE = bis(naphthylphenylphosphino)ethane, in particular the diastereoisomer (-)-BNPE of the formula

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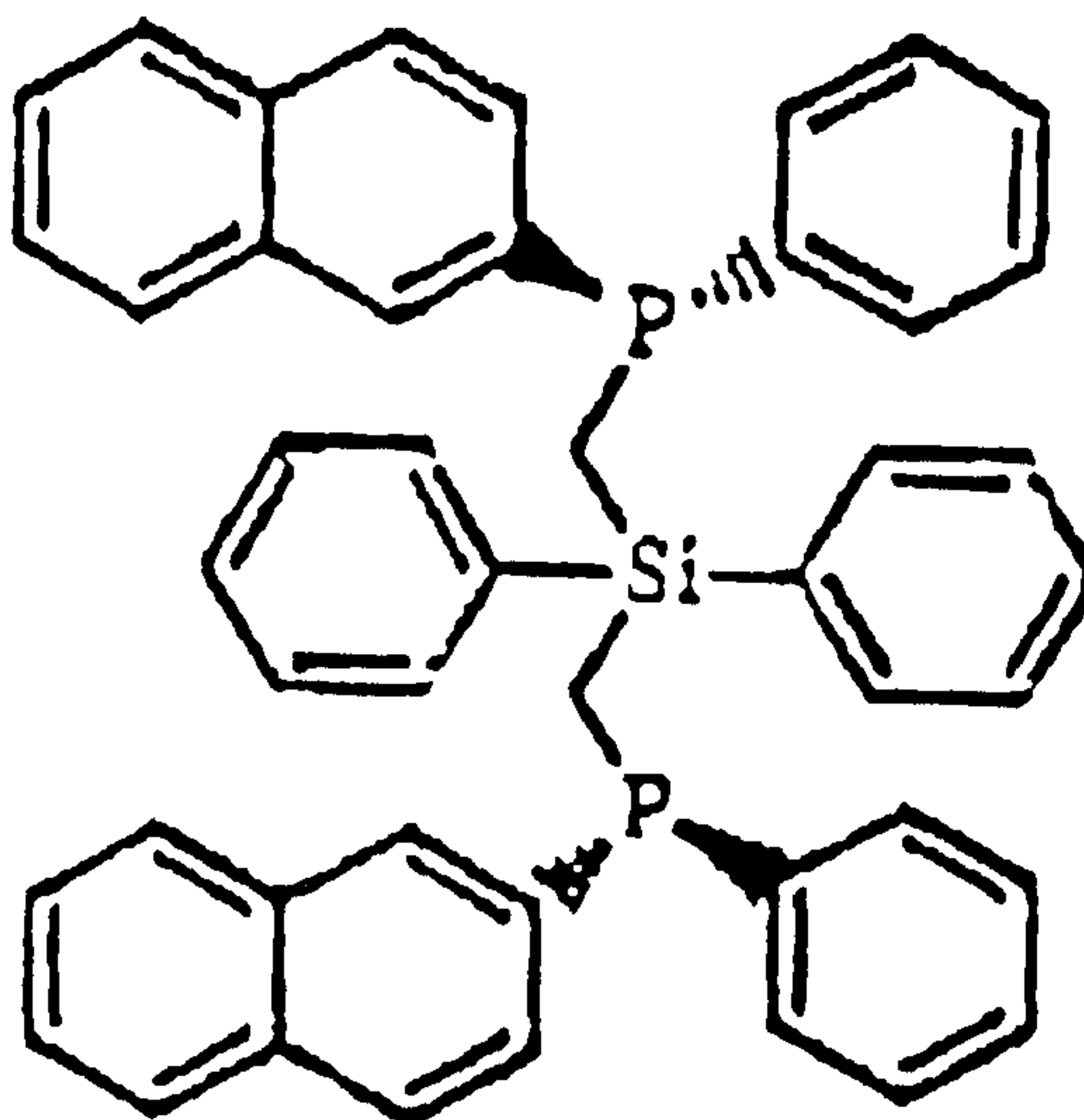


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BNPPMDS = bis(2-naphthylphenylphosphinomethano)di-
phenylsilane, in particular the diastereo-
isomer of the formula

20

25



30

Bu = n-butyl

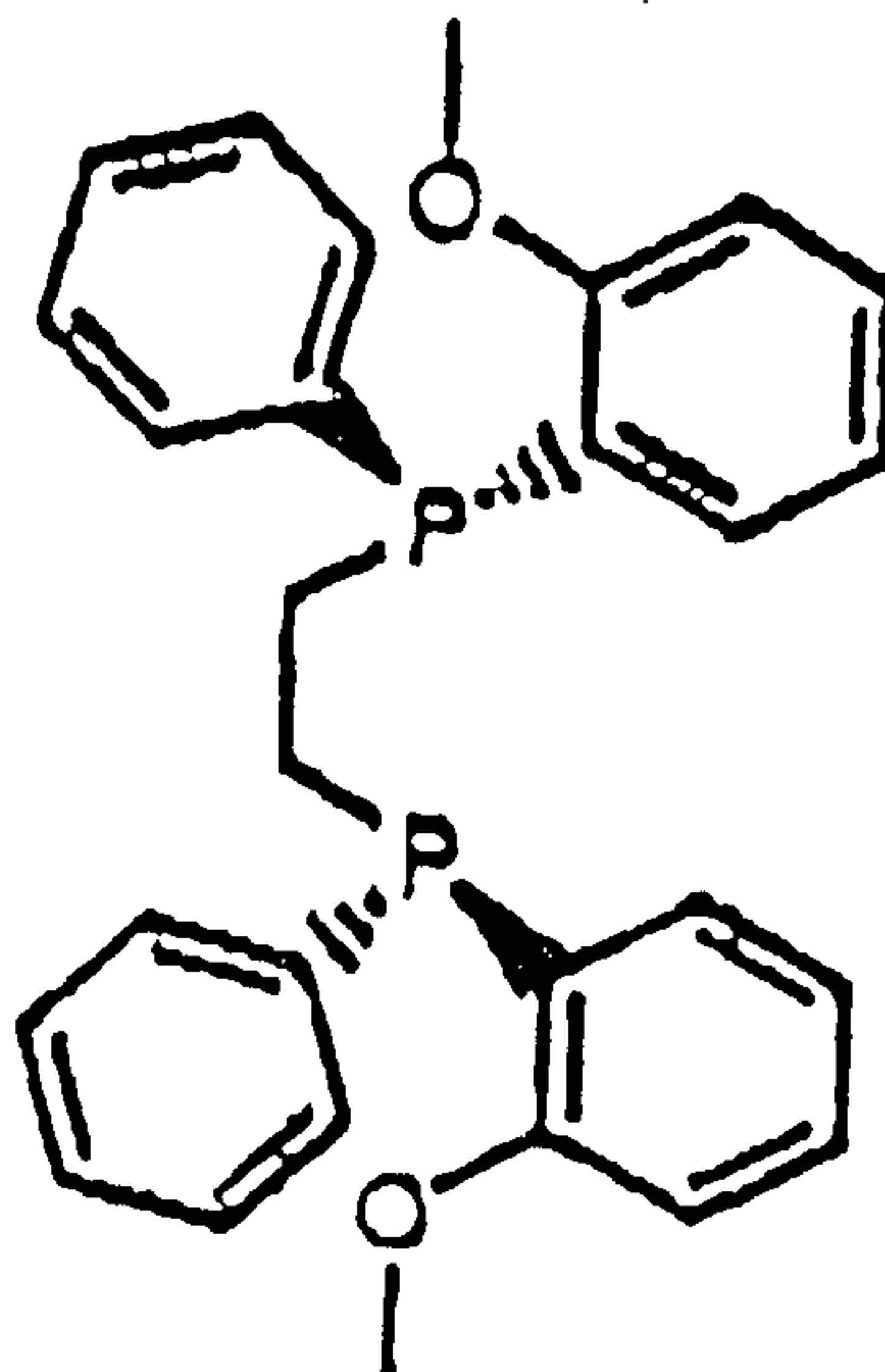
Bz = benzyl

DIPAMP = 1,2-bis(phenyl-o-anisylphosphino)ethane, in
particular the diastereoisomer (-)-DIPAMP of
the formula

35

05

10



15

which is also called (R,R)-1,2-bis(phenyl-ortho-anisylphosphino)ethane

Et	= ethyl
i-Pr	= isopropyl
Me	= methyl
MeO	= methoxy
20 M.p.	= melting point
NMR	= nuclear magnetic resonance
oAn	= ortho-anisyl
Ph	= phenyl
Pr	= n-propyl
25 s-Bu	= sec-butyl
t-Bu	= tert-butyl
THF	= tetrahydrofuran

30

DETAILED DESCRIPTION OF THE INVENTION

C_1 - C_4 -Alkoxy, CN, CF_3 , F, Cl, Br and I groups may be mentioned among the functional groups which are included in the definitions of R^1 and R^2 and which are suitable according to the invention. Thus R^1 and R^2 can contain one or more substituent groups selected from C_1 - C_4 -alkoxy, CN, CF_3 , F, Cl, Br, I and mixtures

35

thereof. Preferably, "functional" groups will be substituted on the aryl fragment of the aryl and aralkyl groups of R^1 and R^2 .

05 The hydrocarbon chain of the bridge Z is either an unsaturated hydrocarbon chain or a saturated hydrocarbon chain.

Said bridge Z will preferably have one of the following structures:

- 10 (a) $-(CH_2)_n-$ and
(b) $-(CH_2)_m-A-(CH_2)_p-$
in which

n, m and p, which are identical or different, are each an integer from 1 to 6, and

15 A is O, S, PR, SiR_2 or NR, in which R is C_1-C_4 -alkyl, C_5-C_6 -cycloalkyl, C_6-C_{10} -aryl, benzyl or phenethyl.

More advantageously, said bridge Z will be selected from the group consisting of

- (a1) $-CH_2-$,
20 (a2) $-CH_2CH_2-$,
(b1) $-CH_2-O-CH_2-$,
(b2) $-CH_2-S-CH_2-$,
(b3) $-CH_2-P(Ph)-CH_2-$,
(b4) $-CH_2-Si(Me)_2-CH_2-$,
25 (b5) $-CH_2-Si(Ph)_2-CH_2-$,
(b6) $-CH_2-Si(Bz)_2-CH_2-$,
(b7) $-CH_2-Si(Et)_2-CH_2-$ or
(b8) $-CH_2CH_2-P(Ph)-CH_2CH_2-$.

30 Among these last bridges Z, the ones which are most valuable according to the invention are those containing a silyl group, namely the bridges of structures (b4) to (b7).

When R^3 is an alkoxy group, it preferably contains 1 to 6 carbon atoms.

35 The general method of preparing a phosphinite-

borane compound of formula I₀ comprises the reaction of a phosphinite material substituted by BH₃ (i.e. an organometallic compound containing phosphorus and derived from a phosphinite product) of the formula

05



10

in which

R¹ and R² are defined as indicated above, and Z¹ is Z or a first fragment of said bridge Z, with a phosphinite compound substituted by BH₃ of the formula

15



20

in which

R¹ and R³ are defined as indicated above, and Z² is R² or the second remaining fragment of the bridge Z, Z¹ and Z² being such that Z¹-Z² = Z.

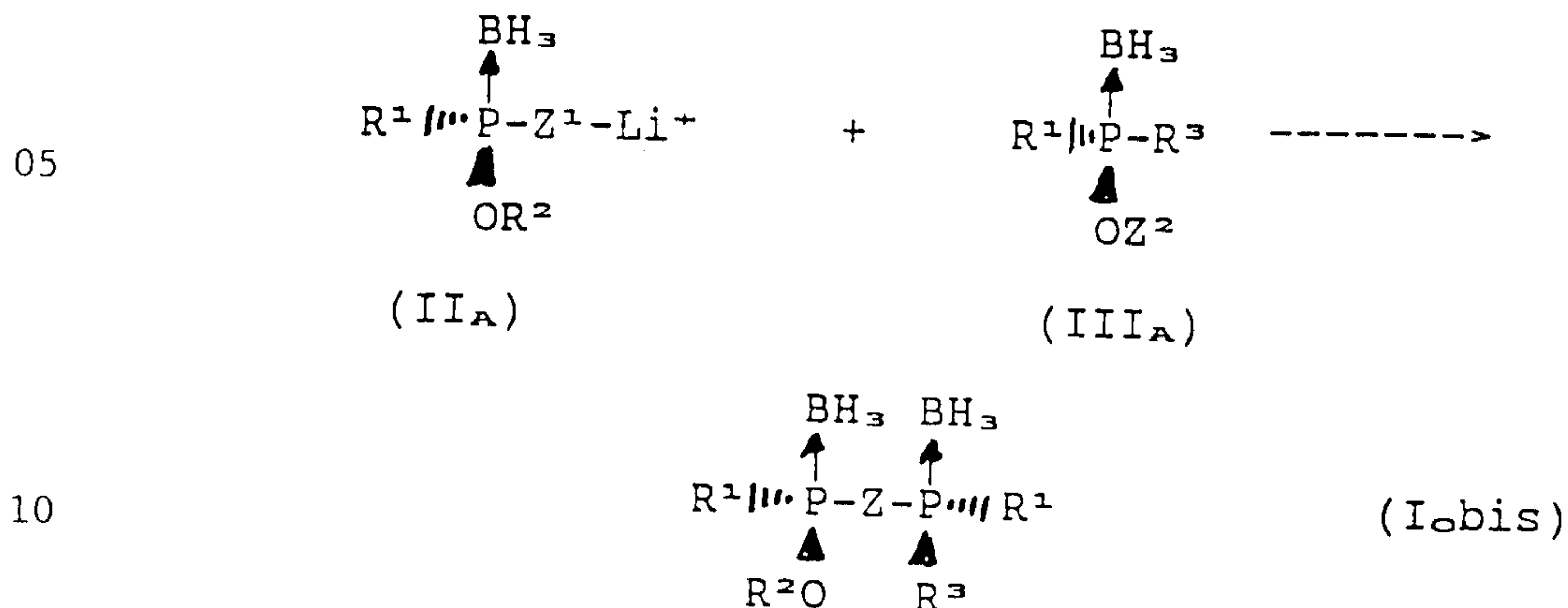
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From a chiral point of view, the reaction of II_A with III_A can be illustrated by the following reaction mechanism:

30

35

Scheme 1



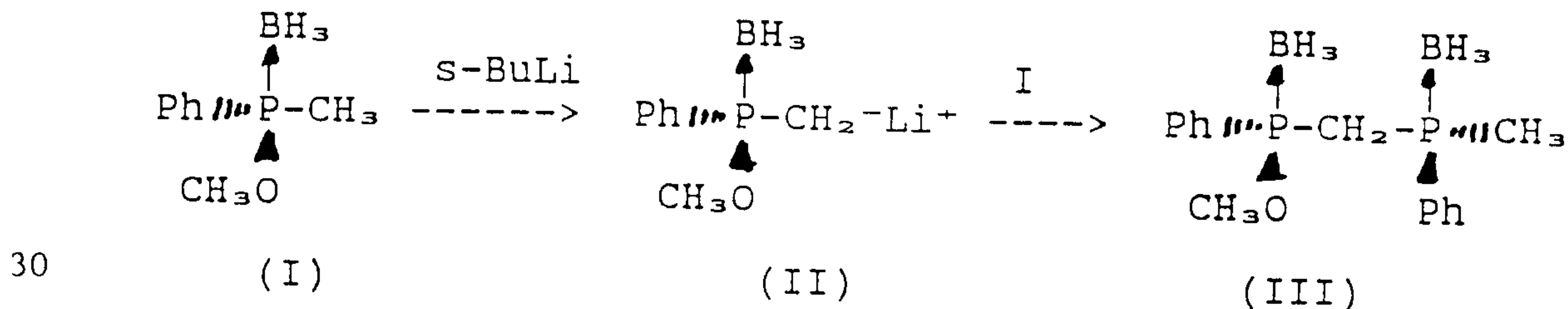
15 More precisely, the counterion of Li^+ , namely X^- , is a halide anion such as F^- , Cl^- or Br^- , the preferred halide anion being Cl^- .

In a first embodiment, structure (a1) given above, i.e. where $\text{Z} = \text{CH}_2$, is obtained by the reaction of one mol of II_A (where Z^1 is CH_2) with at least one mol of III_A (where OZ^2 is OMe).

20 This first embodiment is illustrated by the following reaction mechanism, in which Z^1 is CH_2 , R^1 is Ph , R^2 is Me and R^3 is Me :

Scheme 2

25

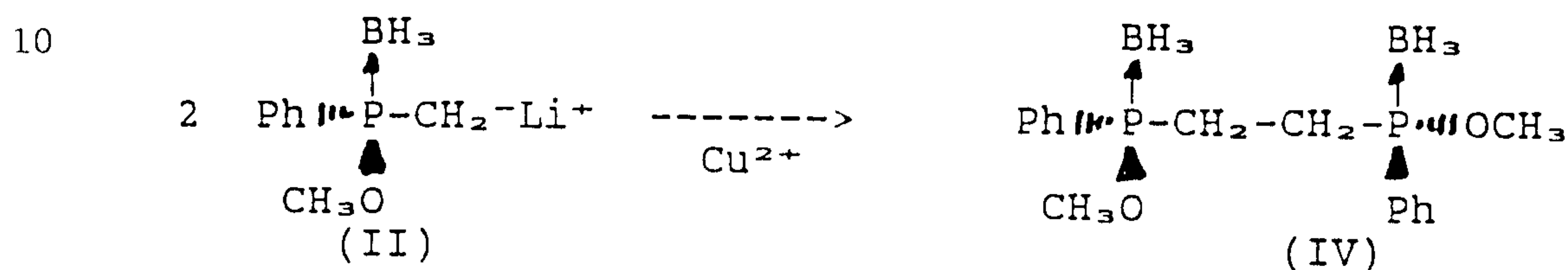


35 In a second embodiment, structure (a2) given above, i.e. where $\text{Z} = \text{CH}_2\text{CH}_2$, is obtained by the reaction of one mol of a compound II_A (where Z^1 is CH_2) with one mol of the same compound II_A (where Z^1 is also

CH₂) in the presence of a mild oxidizing agent, preferably CuX₂ (where X is a halogen atom as defined above, advantageously Cl).

This second embodiment is illustrated by the following reaction mechanism, in which R¹ is Ph, R² is Me, R³ is Me, Z¹ is CH₂ and Z is CH₂CH₂:

Scheme 3



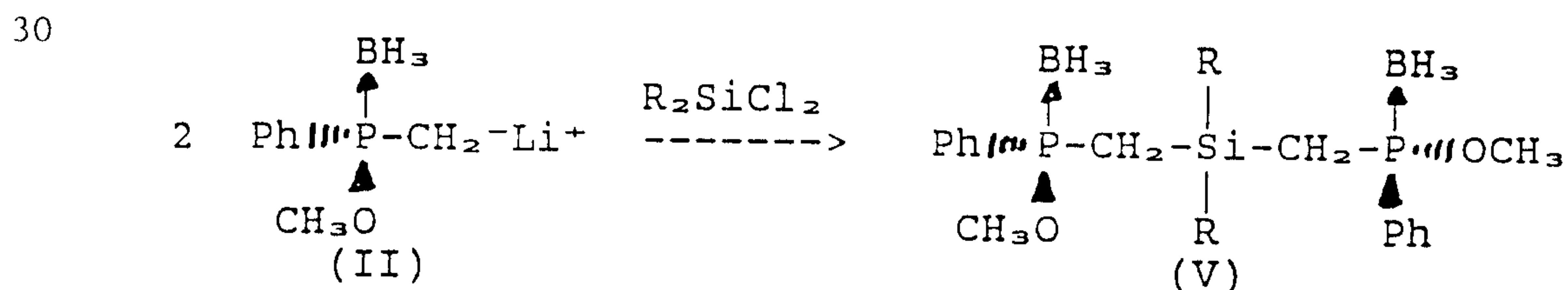
In a third embodiment, structures (b1-b7) given above can be obtained by the reaction of two mol of II_A (where Z¹ is CH₂) with one mol of a dihalogenated compound of the formula



where R, A and X are defined as indicated above.

This third embodiment is illustrated by the following reaction mechanism, in which R¹ is Ph, R² is Me, R³ is Me, Z¹ is CH₂ and Z is CH₂-SiR₂-CH₂ in the final product:

Scheme 4



In the first, second and third embodiments, the reaction is carried out at a temperature of -100°C to $+30^{\circ}\text{C}$. In the first embodiment, a temperature gradient of -40°C to $+15^{\circ}\text{C}$ can be used. In the second embodiment, a temperature gradient of -40°C to $+20^{\circ}\text{C}$ can be used. In the third embodiment, a temperature gradient of -40°C to 0°C can be used.

The preferred reaction solvent for carrying out the first, second and third embodiments is anhydrous THF.

The preferred temperature for carrying out the first, second and third embodiments is 0°C .

Furthermore, from a chiral point of view, an oxy group OR^2 or R^3 , or both, can be replaced in formula I_0 or I_0 bis with a group permitting nucleophilic substitution, i.e. a group which is more nucleophilic than said oxy groups OR^2 and R^3 . For a replacement of this type, see the methods given especially in Examples 4 and 5 below.

BEST MODE

In the best mode of carrying out the invention, chiral compounds of formula I_0 (i.e., more precisely, of formula I_0 bis) are provided in which R^1 is Ph, Ph substituted by one to three alkoxy groups, where each alkoxy group contains from 1 to 4 carbon atoms, or 2-naphthyl, R^2 is a C_1 - C_6 -alkyl group, R^3 is a C_1 - C_6 -alkoxy group and Z is

$-\text{CH}_2-\text{Si}(\text{Me})_2-\text{CH}_2-$,
 $-\text{CH}_2-\text{Si}(\text{Ph})_2-\text{CH}_2-$,
 $-\text{CH}_2-\text{Si}(\text{Bz})_2-\text{CH}_2-$ or
 $-\text{CH}_2-\text{Si}(\text{Et})_2-\text{CH}_2-$.

These compounds are obtained in accordance with the reaction mechanism of scheme 4 given above.

Moreover, these compounds can be converted to

other chiral products, namely, in particular,

(i) phosphinite-borane compounds of formula I_o bis,

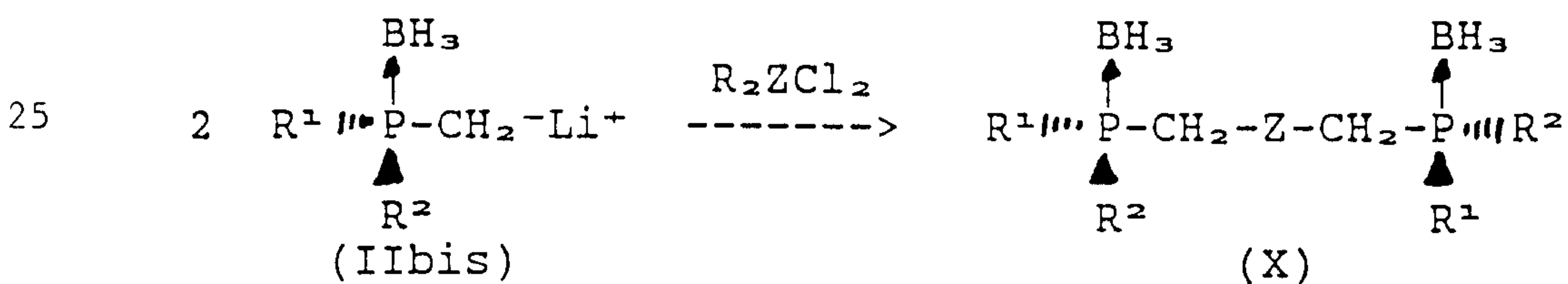
(ii) diphosphine-diborane compounds of formula X and

(iii) diphosphine compounds of formula IX, starting from said compounds of formula X.

The conversions (i) and especially (ii) referred to above are advantageously carried out according to a nucleophilic substitution mechanism, the oxy groups OR² and R³ being replaced in particular with aryl groups, alkoxy-substituted aryl groups and alkyl groups.

In another embodiment of the invention, the diphosphine-diborane compounds can be synthesized directly in accordance with scheme 5 below, which relates to products having a bridge Z consisting of a heterohydrocarbon chain of the structure CH₂-A-CH₂ (where A is defined as indicated above and is advantageously SiR₂).

Scheme 5



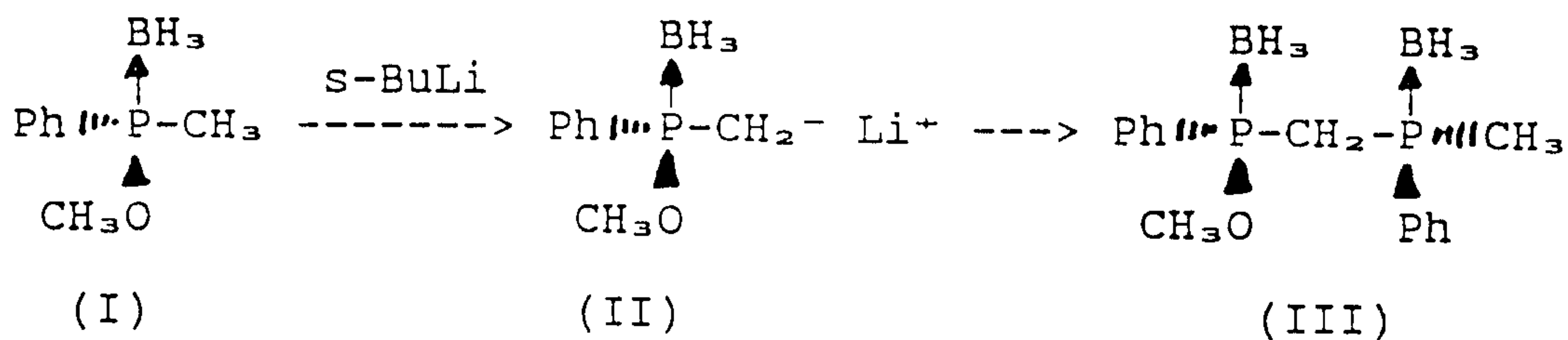
The compounds of formula X which are preferred according to the invention are those in which Z is a bridge

-CH₂-Si(Me)₂-CH₂-,
 -CH₂-Si(Ph)₂-CH₂-,
 -CH₂-Si(Bz)₂-CH₂- or
 -CH₂-Si(Et)₂-CH₂-.

Other advantages and characteristics of the invention will be understood more clearly from the following description of Preparatory Examples. The technical data provided in said Preparatory Examples do not in any way imply a limitation but are given by way of illustration.

Example 1: Methyl (1R,3R)-(-)-[methylphenylphosphino]-methylphenylphosphinite-diborane

10



15

In a 50 ml round-bottomed flask, 2 mmol of phosphinite-borane I are dissolved in 3 ml of anhydrous THF at -78°C and under an inert atmosphere. 2 mmol of sec-butyllithium are added to this solution, with stirring. 0.25 h after this addition, the temperature of the reaction medium is brought slowly to -40°C and the temperature is kept at -40°C for 0.5 h to allow the anions II to form. After this time, a further 2 mmol of phosphinite-borane I are added, the temperature is raised slowly to +15°C and the reaction medium is then left at this temperature for 2 h. After hydrolysis, evaporation of the solvent and washing with water, the expected product is extracted with CH₂Cl₂ and purified by filtration on silica using toluene as the eluent. Yield 70%

20

The characteristics of the product obtained are as follows:

Colorless oil

35

[α] = -56° (c = 1; CHCl₃)

^1H NMR (CDCl_3):

major signals: $\delta = 0.1-1.5$ (6H, qb, $^1J_{\text{BH}} = 80$); 1.83 (3H, d, $J = 10.2$); 2.60 (2H, m); 3.61 (3H, d, $J = 12.5$); 7.25-7.5 (6H, m); 7.5-7.8 (4H, m)

05 minor signals: $\delta = 1.56$ (3H, d, $J = 10.38$); 3.35 (3H, d, $J = 11.8$)

^{13}C NMR (CDCl_3): $\delta = 11.39$ (d, $J = 39$); 30.19 (dd, $J = 23$, $J = 32$); 54.01 (s); 128.47-132.36 (aromatic) (minor signal: $\delta = 12.89$ (d, $J = 39$))

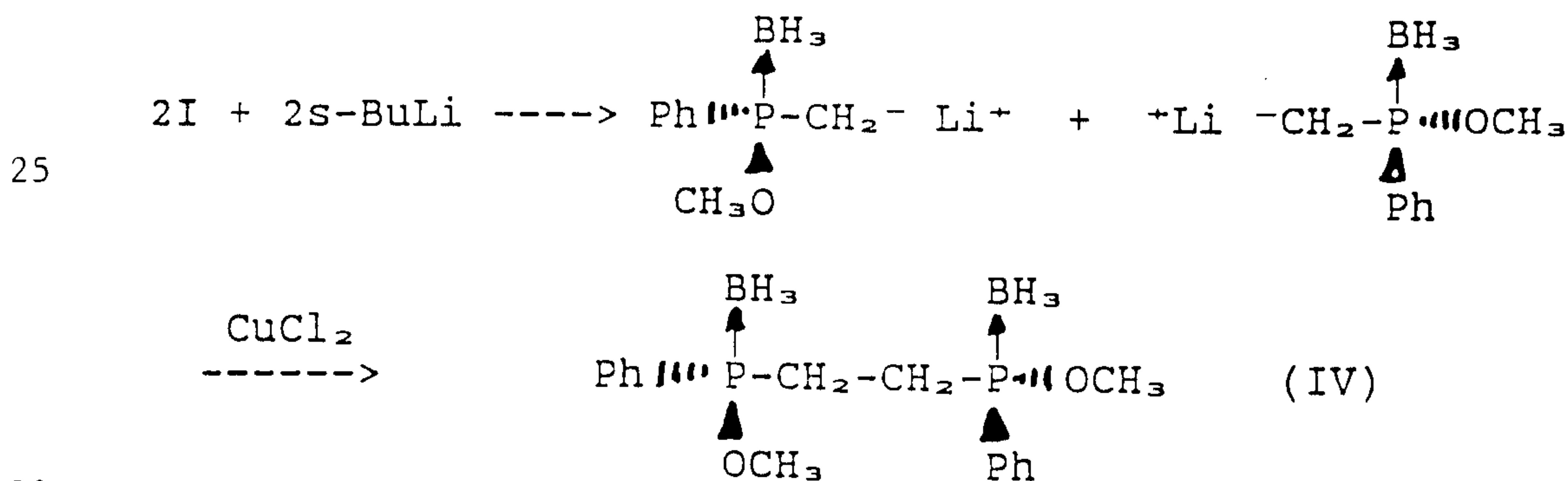
10 ^{31}P NMR (CDCl_3): $\delta = +8.38$ (q, $^1J_{\text{PB}} = 67.5$); +113.10 (q, $^1J_{\text{PB}} = 69.8$)

IR (pure): $\nu = 3057$; 2945 (C-H); 2385; 2254 (B-H); 1437; 1417; 1173; 1115; 1064; 1034

Microanalysis for: $\text{C}_{15}\text{H}_{24}\text{O}_{11}\text{B}_2\text{P}_2$

15		calculated	found
	molecular weight	304.1332	304.1334
	%C	59.21	58.01
	%H	7.89	7.72

20 Example 2: (S,S)-1,2-bis[Methoxyphenylphosphino]ethane-borane



In a 50 ml round-bottomed flask, 2 mmol of phosphinite-borane I are dissolved in 3 ml of anhydrous THF at -78°C and under an inert atmosphere. 2 mmol of sec-butyllithium are added to this solution, with

stirring. 0.25 h after this addition, the temperature of the reaction medium is brought slowly to -40°C and the temperature is kept at -40°C for 0.5 h to allow the anions II to form. After this time, 10 mmol of CuCl_2 are added and the mixture is left to stand in air for 12 h. After hydrolysis, evaporation of the solvent and washing with water, the product is extracted with CH_2Cl_2 and purified by filtration on silica using toluene as the eluent.

Yield 88%

M.p. = $111-115^{\circ}\text{C}$

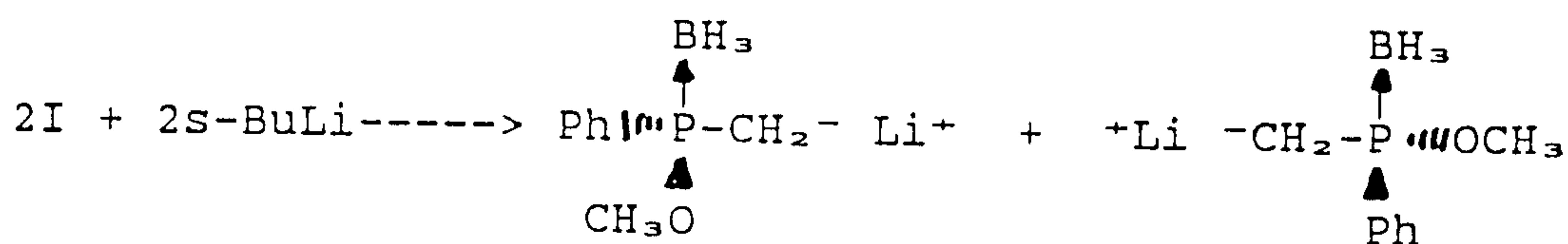
^{31}P NMR = +118 ($J_{\text{PB}} = 58 \text{ Hz}$)

$[\alpha]_{\text{D}} = -115.1^{\circ}$ ($c = 1$; CHCl_3)

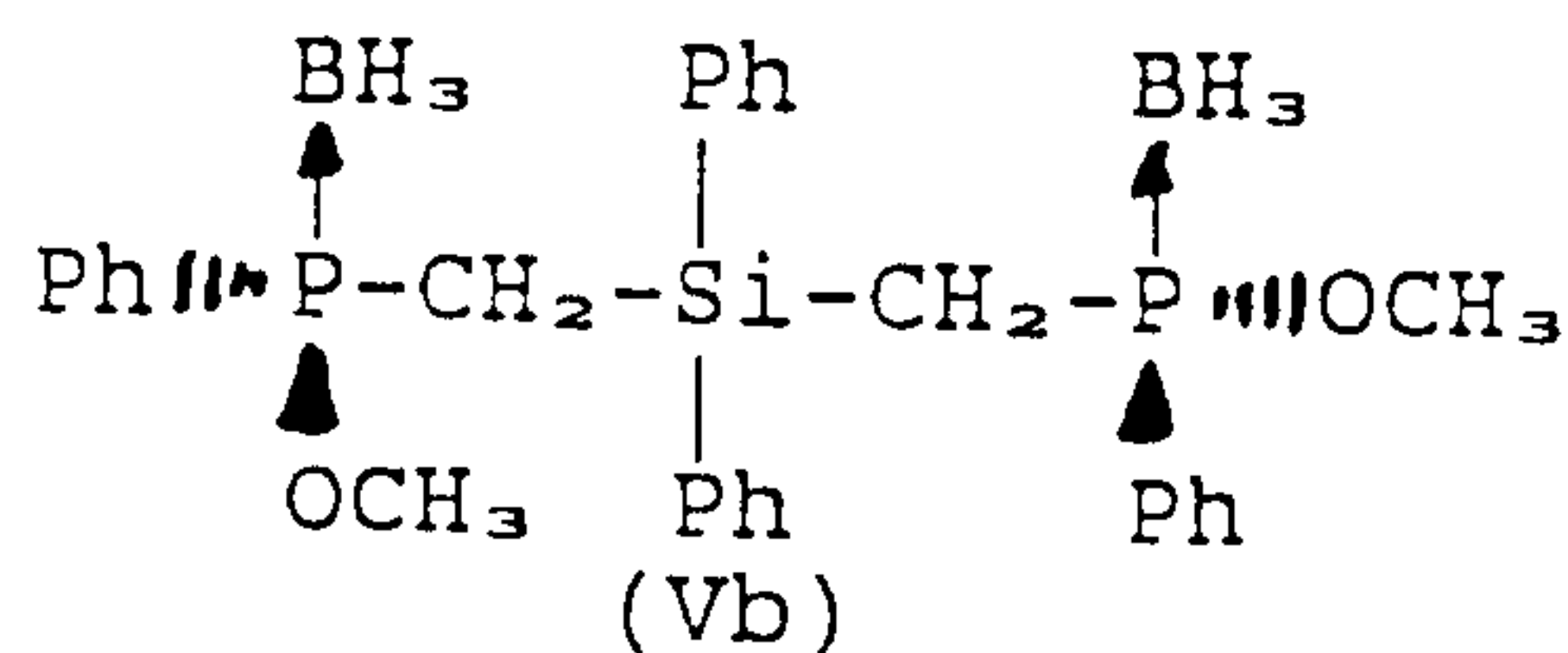
^1H NMR = 0-1.5 (6H, m); 1.9-2.4 (4H, m); 3.6 (6H, d); 7.4-7.8 (10, m)

IR: $\nu_{\text{BH}} = 2370 \text{ cm}^{-1}$

Example 3: (R,R)-bis[(Methoxyphenylphosphino)methyl]-diphenylsilyl-borane



Ph_2SiCl_2



In a 50 ml round-bottomed flask, 2 mmol of phosphinite-borane I are dissolved in 3 ml of anhydrous THF at -78°C and under an inert atmosphere. 2 mmol of s-butyllithium are added to this solution, with stirring. After 0.25 h, the temperature is brought slowly to -40°C and left for 0.5 h at -40°C to allow the anions II to form. After this time, 1 mmol of dichlorodiphenylsilane is added and the temperature is raised slowly to 0°C and then kept for 2 h at 0°C . After hydrolysis, evaporation of the solvent and washing with water, the product is extracted with CH_2Cl_2 and purified by filtration on silica using toluene as the eluent.

Yield 90%

Thick colorless oil

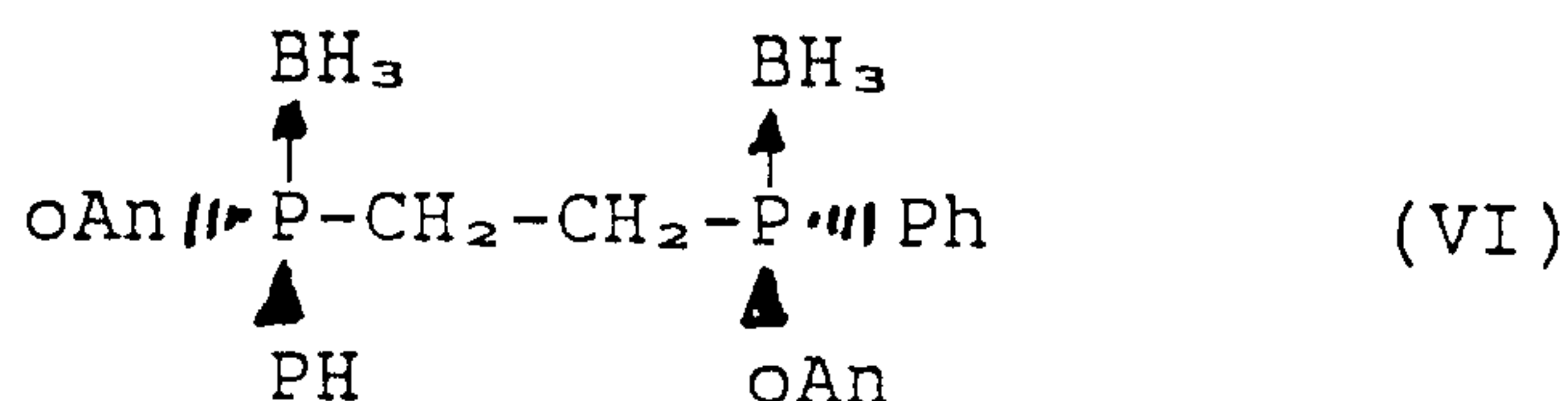
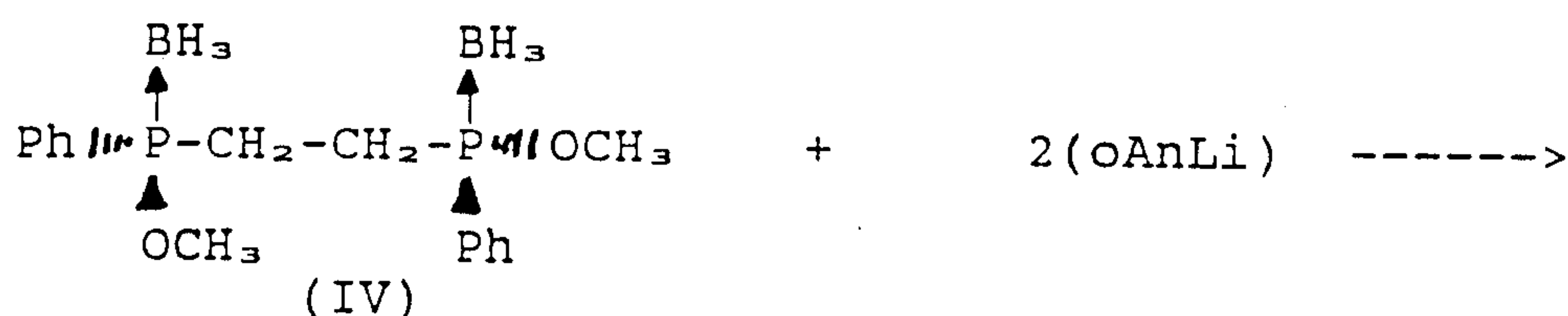
^1H NMR (CDCl_3): $\delta = 0.0-1.5$ (6H, qb, $^1J_{\text{BH}} = 95$); 2.13-2.43 (4H, qd, $J = 7.7$, $J = 16.4$); 3.28 (6H, d, $J = 12.28$); 7.05-7.85 (20H, m)

(other diastereoisomer: 3.25 (6H, d, $J = 12.27$))

^{31}P NMR (CDCl_3): $\delta = +116.74$ (m)

(other isomer: $\delta = +114$ (m))

Example 4: Use of the diphosphinite-borane IV of Example 2 in the preparation of DIPAMP-borane VI

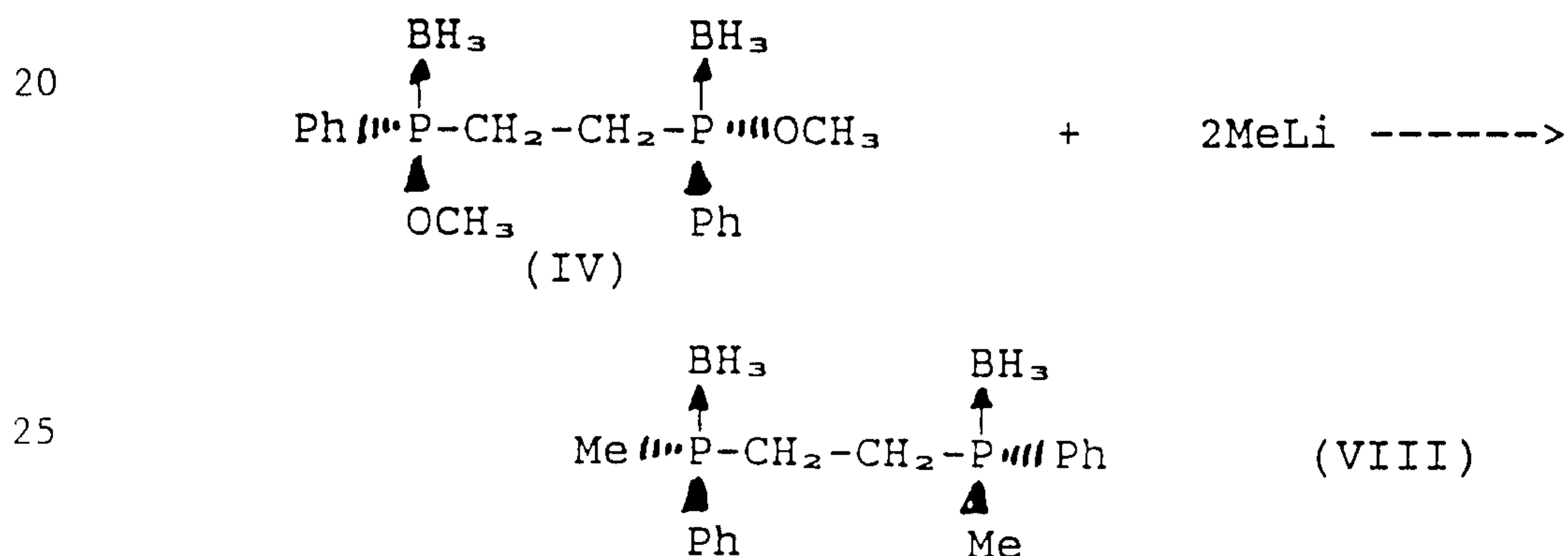


In a 50 ml round-bottomed flask, 2 mmol of phosphinite-borane IV are dissolved in 5 ml of anhydrous THF at -78°C and under an inert atmosphere. 2.1 mmol of o-anisyllithium (oAnLi) are added to this solution, with stirring. 0.25 h after this addition, the temperature of the reaction medium is brought slowly to 0°C over 2 h and the mixture is hydrolyzed. After evaporation of the solvent, washing with water and extraction with CH_2Cl_2 , the product obtained is purified by filtration on silica using toluene as the eluent.

Yield 80%

M.p. = 163°C (consistent with the literature)

Example 5: Use of the diphosphinite-borane IV of Example 2 in the preparation of diphosphine-borane VIII



In a 50 ml round-bottomed flask, 2 mmol of diphosphinite-borane IV are dissolved in 5 ml of anhydrous THF at -78°C and under an inert atmosphere. 2.1 mmol of methyllithium are added to this solution, with stirring. 0.25 h after this addition, the temperature of the reaction medium is brought slowly to 0°C over 2 h and the mixture is hydrolyzed. After evaporation

of the solvent, washing with water and extraction with CH_2Cl_2 , the product obtained is purified by filtration on silica using toluene as the eluent.

Yield 90%

05 M.p. = 166-168°C

IR: 2378, 1457, 1420, 1065 cm^{-1}

^1H NMR: 0-2 ppm (6H, m); 1.55 (6H, m); 1.8-2.2 (4H, m); 7.2-7.9 (10H, m)

Analysis for: $\text{C}_{16}\text{H}_{26}\text{B}_2\text{P}_2$

10 calculated: C = 63.58% H = 8.61%

found: C = 63.68% H = 8.55%

Example 6: Use of the diphosphine-boranes prepared in Examples 4 and 5 in the preparation of diphosphines

15

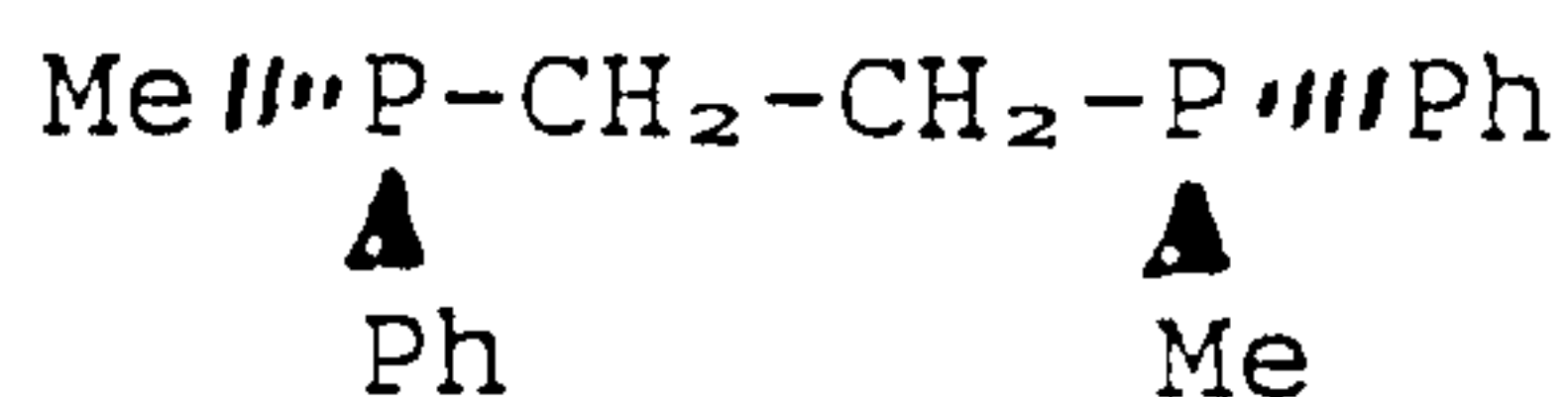
According to the technique described in the prior art by T. Imamoto (this is the technique used in scheme 3, page 6358, of the article by S. JUGE et al. cited above), a 0.5 M solution of (-)-DIPAMP-diborane VI is heated at 50°C for 12 h. After this time, the excess amine is evaporated off and the residue is filtered on a short silica column using toluene as the eluent. The expected diphosphine, namely the product (-)-DIPAMP in the case in question, is recovered in the first fractions. M.p. = 103°C (consistent with the literature).

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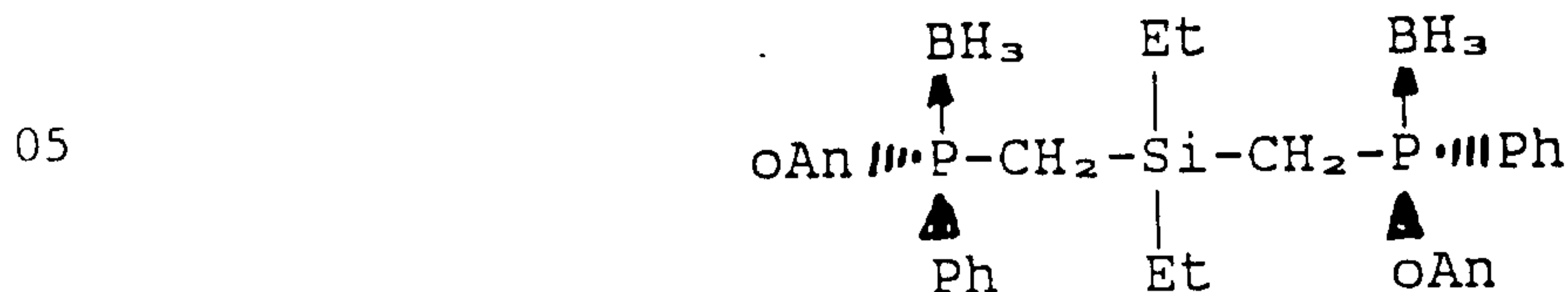
If the compound of formula VIII obtained according to Example 5 above is used as the starting material, the expected diphosphine, namely the compound of the formula

30



35 is obtained analogously.

Example 7: (R,R)-bis[(o-Anisylphenylphosphino)methyl]-
diethylsilyl-diborane



10 Scheme 5 is followed using a procedure similar
to that described in Example 3 above.

2 mmol of diphosphine-diborane are dissolved in
3 ml of anhydrous THF at -70°C and under an inert
atmosphere. 2 mmol of s-BuLi are added to the resul-
ting solution, with stirring. After the reaction
15 medium has been stirred for 0.25 h, the temperature is
brought slowly to -40°C and kept at -40°C for 0.5 h to
allow the anions to form. After this time, 1 mmol of
dichloroethylsilane is added and the temperature is
raised slowly to 0°C and kept for 2 h at 0°C . After
20 hydrolysis, evaporation of the solvent and washing with
water, the product is extracted with CH_2Cl_2 and puri-
fied by filtration on silica using toluene as the
eluent. Recrystallization from ethanol gives the
expected product in the form of white crystals.

25 Yield 76%

M.p. = 181°C

$[\alpha]_D = +86^\circ\text{C}$

^1H NMR (CDCl_3): 0-1.5 (16H, m); 1.7-2.4 (4H, m); 3.7
(6H, s); 6.8-8 (18H, m)

30 ^{13}C NMR (CDCl_3): 5.23; 6.7; 30.8; 55.1; 110.9; 120.7-
135.9; 161

IR (KBr): 698; 747; 764; 781; 805; 1227; 1464; 1589;
2375

Example 8: (R,R)-bis[(2,4-Dimethoxyphenylphenylphosphino)methyl]diphenylsilyl-diborane

The expected product is obtained with a yield of 92% by following the modalities described in Example 7 above.

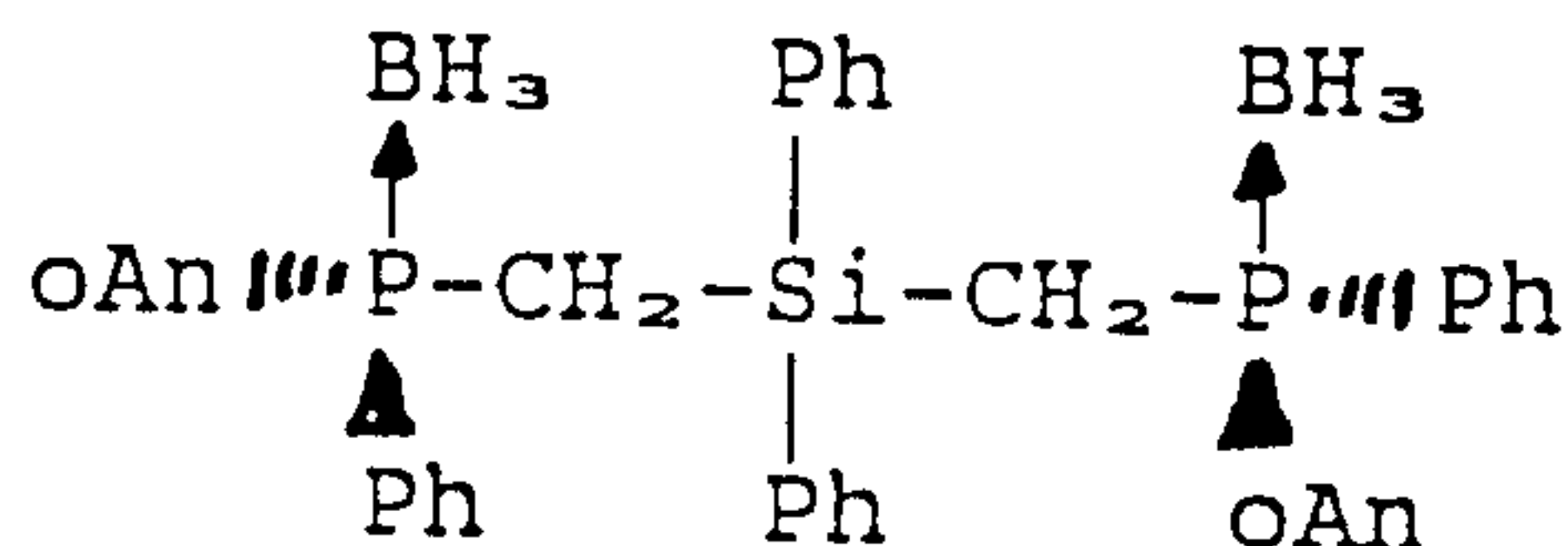
M.p. = 154°C

$[\alpha]_D = +61^\circ$

^1H NMR (CDCl_3): 0-1.5 (6H, m); 2.6-2.9 (4H, m); 3.49 (6H); 3.78 (6H, s); 6.1-6.3 (2H, m); 6.9-7.7 (24H, m)

^{13}C NMR (CDCl_3): 55.2 ($J_{\text{PC}} = 18 \text{ Hz}$); 98.4; 105; 126-135; 160-161

Example 9: (R,R)-bis[(o-Anisylphenylphosphino)methyl]diphenylsilyl-diborane



The expected product is obtained with a yield of 85%, after recrystallization from a hexane/toluene mixture (2/1 v/v), by following the modalities described in Example 7 above.

M.p. = 200°C

^1H NMR (CDCl_3): 0-1.8 (6H, m); 2.85 (4H, d); 3.5 (6H, s); 6.5-7.5 (28H, m); 8 (d)

^{13}C NMR (CDCl_3): 55; 110; 115-137 (m)

IR (KBr): 689; 803; 1021; 1124; 1249; 1430; 1625; 2382

Example 10: (S,S)-bis[(o-Anisylphenylphosphino)methyl]dimethylsilyl-diborane

If the starting material is o-anisylmethylphenylphosphine-borane [i.e. (S)-PAMP-BH₃], the expected product is obtained with an enantiomeric efficiency

(abbreviated to e.e.) of 100%, after recrystallization from hexane, by following the modalities described in Example 7 above.

M.p. = 139-140°C

05 Rf (in toluene) = 0.4

¹H NMR (CDCl₃): 0.2 (6H, s); 0.5-1.9 (6H, qb, ¹J_{BH} = 48.6); 1.8 (2H, t, J = 13.5); 2.39 (2H, dd, J = 13.8, J = 18.2); 3.8 (6H, s); 6.95-8.18 (18H, m)

10 ¹³C NMR (CDCl₃): 11.14 (d, J = 27); 55.23 (s); 111.05 (s); 117.76-161.36

³¹P NMR (CDCl₃): +12.4 (dm, J = 56)

IR (KBr): 1017; 1074; 1105; 1130; 1249; 1276; 1431; 1478; 1589; 2365 (B-H); 2403; 2972 (C-H); 3052

Analysis for: C₃₀H₄₀O₂¹¹B₂P₂Si

	calculated	found
15 molecular weight	544.2459	544.2435
%C	66.17	66.06
%H	7.35	7.42

20 Example 11: (R,R)-bis[(2-Naphthylphenylphosphino)-methyl]diphenylsilyl-diborane

If the starting materials are (S)-(methyl-2-naphthylphenylphosphine)-borane and dichlorodiphenylsilane, the expected product is obtained with an e.e. of 100%, after recrystallization from a hexane/propanol mixture (1/1 v/v), by following the modalities described in Example 7 above.

M.p. = 188°C

[α]_D = -2° (c = 1; CHCl₃)

30 ¹H NMR (CDCl₃): 0.5-2.0 (6H, qb); 2.65 (4H, dt, J = 14.2, J = 76.6); 6.70-7.88 (32H, m); 7.97 (2H, d, J = 13); 6.70-7.88 (32H, m); 7.97 (2H, d, J = 13)

¹³C NMR (CDCl₃): 10.10 (d, J = 24.2); 126.35-135.21

³¹P NMR (CDCl₃): -12.6 (m)

Example 12: (R,R)-bis[(Methoxyphenylphosphino)methyl]-
dimethylsilyl-diborane

The expected product is obtained with a yield
of 93.7%, after recrystallization from toluene, by
following the modalities described in Example 3 above.

M.p. = 50°C

Rf = 0.7 (in toluene)

$[\alpha]_D = -89^\circ\text{C}$ (c = 1; CHCl_3)

^1H NMR (CDCl_3): 0.13 (6H, s); 0.4-1.8 (6H, qb, $^1J_{\text{BH}} =$
100); 1.53 (4H, ddd, J = 9.5, J = 14.3, J = 59.5); 3.52
(6H, d, J = 11.9); 7.43-7.57 (6H, m); 7.71-7.82 (4H, m)
[other diastereoisomer: 3.48 (6H, d, J = 11.9)]

^{13}C NMR (CDCl_3): 19.40 (d, J = 33.5); 53.32 (s); 128.7
(d, J = 9.6); 130.64 (d, J = 11); 131.97 (s); 132.75
(s)

^{31}P NMR (CDCl_3):

major signal: +116.22 (q, $^1J_{\text{BH}} = 78$)

minor signal: +113.70 (q, $^1J_{\text{BH}} = 70$)

IR (pure): 1032; 1066; 1115; 1255 (C-O); 1437 (P-O);
2378 (B-H); 2841 (C-H); 2944; 3058

Analysis for: $\text{C}_{18}\text{H}_{32}\text{O}_2\text{B}_2\text{P}_2\text{Si}$

	calculated	found
molecular weight	392.1832	392.1786
%C	55.10	55.60
%H	8.16	8.27

Example 13: (R,R)-bis[(o-Anisylphenylphosphino)methyl]-
dimethylsilyl-diborane

The expected product, which is the diastereo-
isomer of the product of Example 10, is obtained with a
yield of 65%, after recrystallization from hexane, by
following the modalities described in Example 7 above.

Example 14: (R,R)-bis[(o-Anisylphenylphosphino)methyl]-diphenylsilyl-diborane and (S,S)-bis[(o-anisylphenylphosphino)methyl]diethylsilyl-diborane

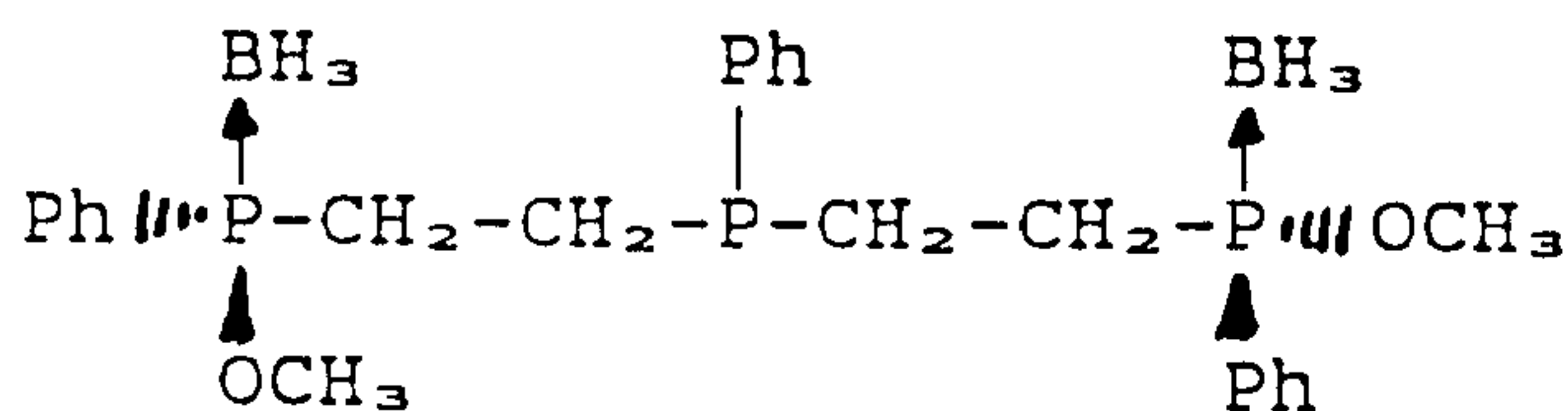
05 These two products are obtained from the diphosphinite-diborane of Example 3 and its diastereoisomer by removing the BH_3 groups present on the phosphorus atoms in accordance with operating modalities analogous to those described in Example 4 above.

10 Starting from the product of Example 3, the product obtained is purified by filtration on silica using toluene as the eluent. After recrystallization from a hexane/toluene mixture (2/1 v/v), said pure product is obtained with a yield of 65%.

15 M.p. = 200°C

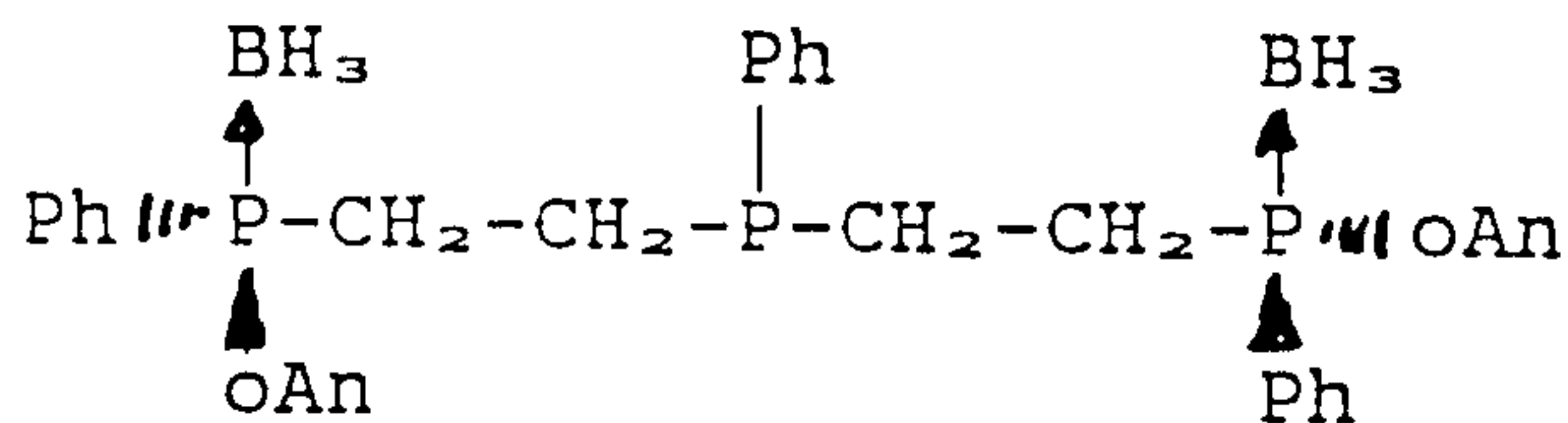
Example 15:

The diborane compound containing three phosphorus atoms of the formula



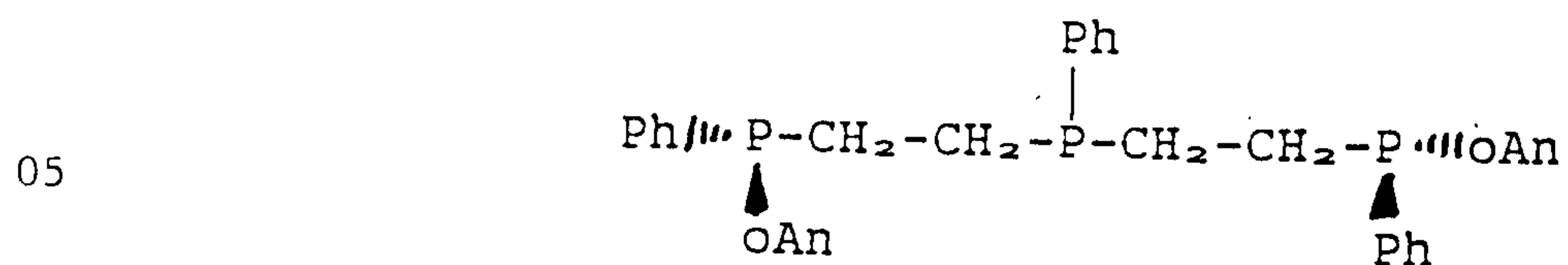
25 is obtained in accordance with scheme 4 by replacing R_2SiCl_2 with $\text{RP}(\text{CH}_2\text{Cl})_2$.

The methoxy group is replaced with a group oAn by nucleophilic substitution to give the compound



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The triphosphine compound of the formula



is obtained by removing the borane groups in accordance with the operating modalities of Example 6.

10

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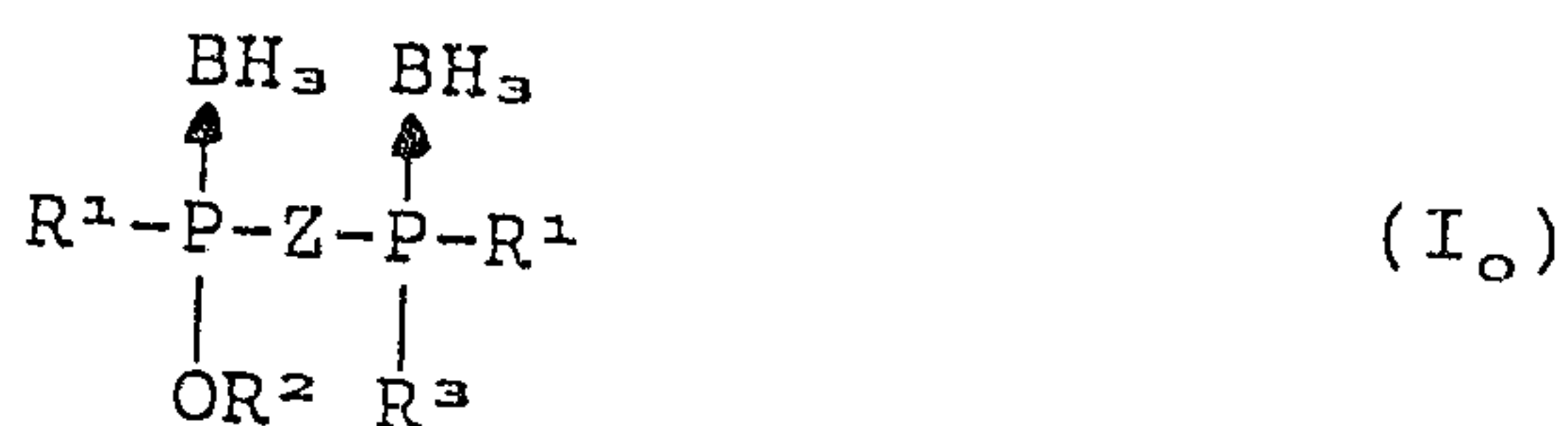
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WHAT IS CLAIMED IS:

1. A phosphinite compound substituted by BH_3 on the phosphorus, which is selected from the group consisting of the phosphinite-borane products of the general formula



in which

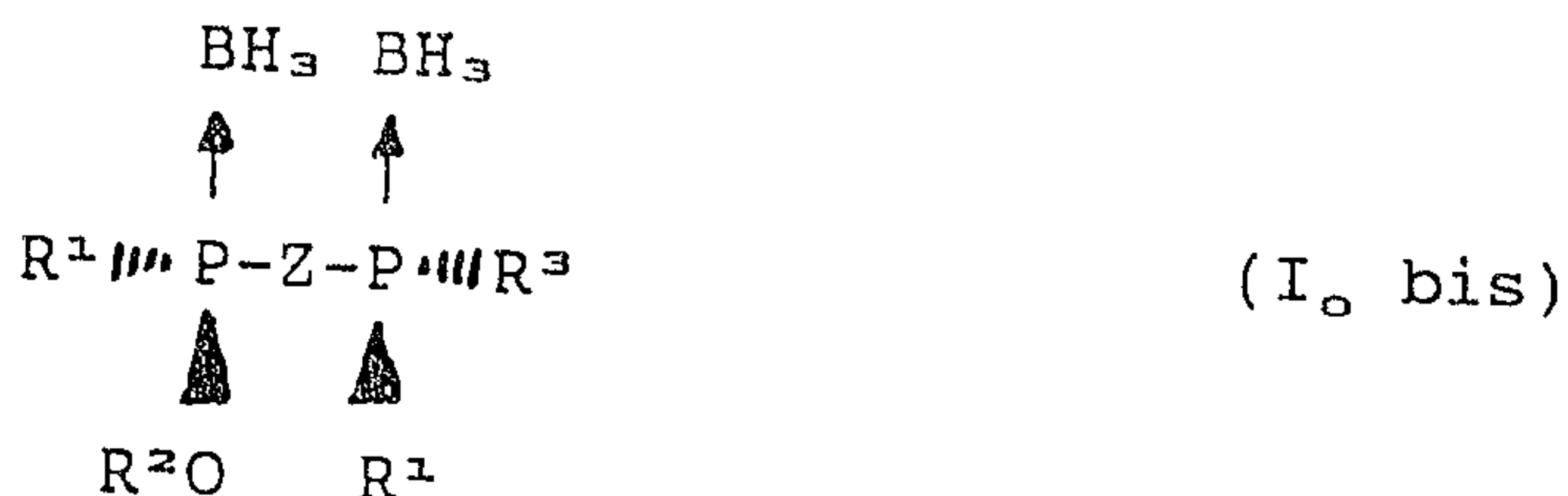
R^1 and R^2 , which are identical or different, are each a C_1 - C_{18} -alkyl group, a C_5 - C_{18} -cycloalkyl group, a C_7 - C_{18} -aralkyl group or a C_6 - C_{14} -aryl group, it being possible for each of these groups to carry functional groups,

R^3 is a C_1 - C_{18} -alkyl, C_5 - C_{18} -cycloalkyl, C_7 - C_{18} -aralkyl, C_6 - C_{14} -aryl, C_1 - C_{18} -alkoxy, C_7 - C_{18} -cycloalkoxy, C_7 - C_{18} -aralkoxy or C_6 - C_{14} -aryloxy group, and

Z is a bridge linking the two phosphorus atoms, said bridge being (i) a hydrocarbon chain having from 1 to 12 catenary C atoms, or (ii) a heterohydrocarbon chain containing from 1 to 12 catenary C atoms and at least one catenary heteroatom selected from O, S, Si, P and N,

with the further condition that (i) Z is other than CH_2 when R^1 = phenyl and $\text{R}^2 = \text{R}^3$ = methyl simultaneously, and (ii) Z is other than CH_2CH_2 when R^1 = phenyl, R^2 = methyl and R^3 = methoxy simultaneously.

2. A phosphinite compound according to claim 1 which has the chiral structure



where R^1 , R^2 , R^3 and Z are defined as indicated above.

3. A phosphinite compound according to claim 1 or 2 in which R^1 and R^2 are each an unsubstituted aryl group or an aryl group monosubstituted or polysubstituted by C_1 - C_4 -alkoxy, CN , CF_3 , F , Cl , Br or I .

4. A phosphinite compound according to claim 1 or 2 in which the bridge Z has one of the following structures:

(a) $-(\text{CH}_2)_n-$ and

(b) $-(\text{CH}_2)_m-\text{A}-(\text{CH}_2)_p-$

in which

n , m and p , which are identical or different, are each an integer from 1 to 6, and

A is O , S , PR , SiR_2 or NR , in which R is C_1 - C_4 -alkyl, C_5 - C_6 -cycloalkyl, C_6 - C_{10} -aryl, benzyl or phenethyl.

5. A phosphinite compound according to claim 1 or 2 in which the bridge Z is selected from the group consisting of

(a1) $-\text{CH}_2-$,

(a2) $-\text{CH}_2\text{CH}_2-$,

(b1) $-\text{CH}_2-\text{O}-\text{CH}_2-$,

(b2) $-\text{CH}_2-\text{S}-\text{CH}_2-$,

(b3) $-\text{CH}_2-\text{P}(\text{Ph})-\text{CH}_2-$,

(b4) $-\text{CH}_2-\text{Si}(\text{Me})_2-\text{CH}_2-$,

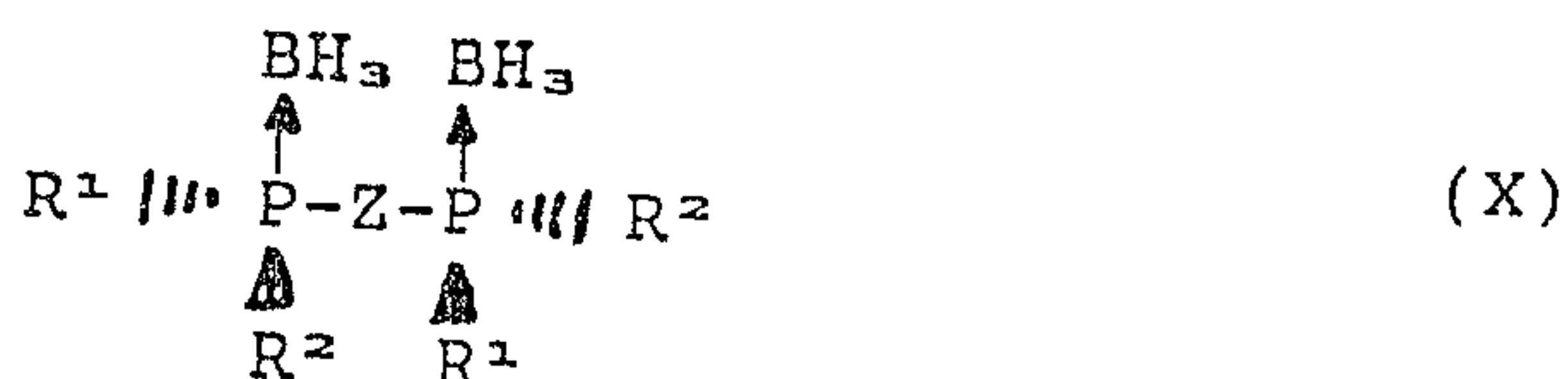
(b5) $-\text{CH}_2-\text{Si}(\text{Ph})_2-\text{CH}_2-$,

(b6) $-\text{CH}_2-\text{Si}(\text{Bz})_2-\text{CH}_2-$,

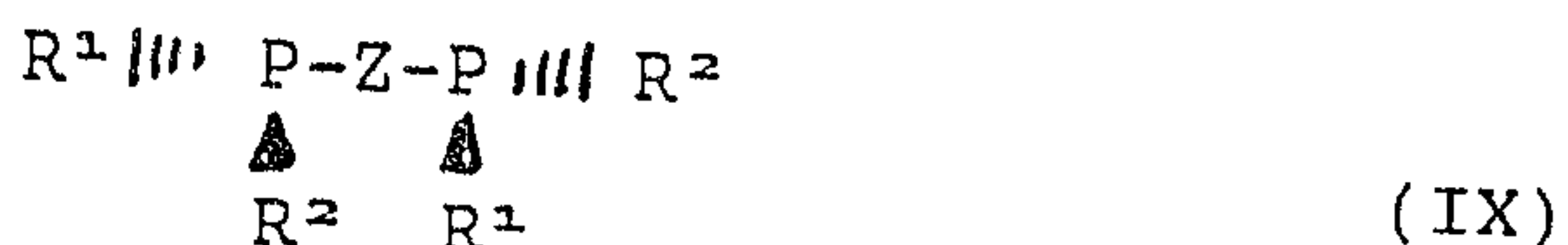
(b7) $-\text{CH}_2-\text{Si}(\text{Et})_2-\text{CH}_2-$ or

(b8) $-\text{CH}_2\text{CH}_2-\text{P}(\text{Ph})-\text{CH}_2\text{CH}_2-$.

6. A phosphinite compound according to claim 1 or 2 in which R^3 is a C_1 - C_6 -alkoxy group.
7. A chiral phosphinite compound of formula I₀ bis according to claim 2 in which R^1 is Ph, Ph substituted by one to three alkoxy groups, where each alkoxy group contains from 1 to 4 carbon atoms, or 2-naphthyl, R^2 is a C_1 - C_6 -alkyl group, R^3 is a C_1 - C_6 -alkoxy group and Z is
- CH₂-Si(Me)₂-CH₂-,
 -CH₂-Si(Ph)₂-CH₂-,
 -CH₂-Si(Bz)₂-CH₂- or
 -CH₂-Si(Et)₂-CH₂-.
8. A chiral phosphinite compound of formula I₀ bis according to claim 2 which is selected from the group consisting of
- (R,R)-bis[(methoxyphenylphosphino)methyl]diphenylsilyl-diborane,
 (R,R)-bis[(methoxyphenylphosphino)methyl]dimethylsilyl-diborane and
 (R,R)-bis[(methoxyphenylphosphino)methyl]diethylsilyl-diborane.
9. A method of preparing a phosphinite-borane compound of formula I₀ or I₀ bis according to claim 1 or 2, said method comprising the reaction of an organometallic compound derived from a phosphinite-borane with a non-organometallic phosphinite-borane compound.
10. Use of a chiral phosphinite-borane compound of formula I₀ bis according to claim 2 in the preparation of a chiral diphosphine product of the formula

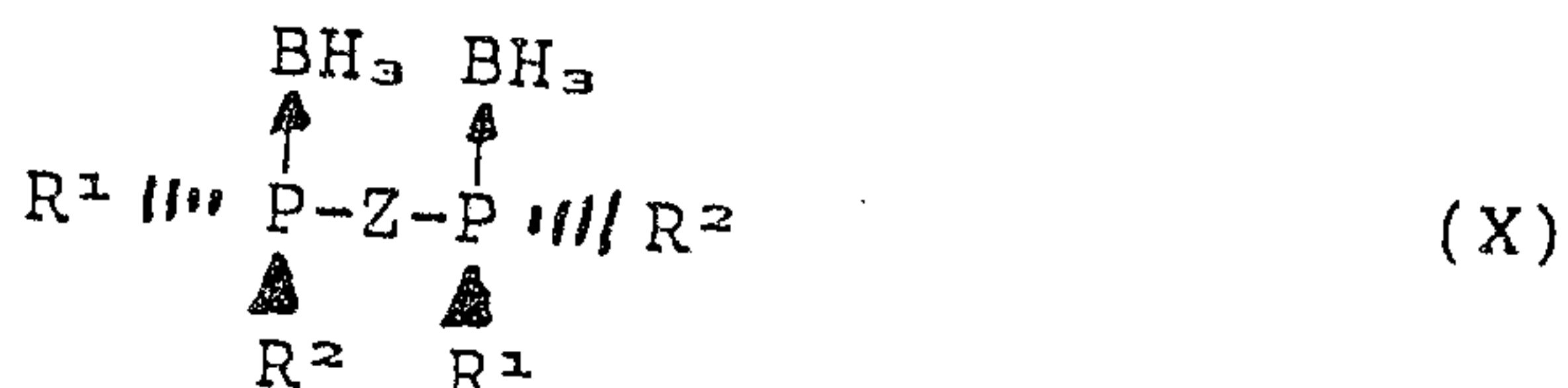


or



where R^1 , R^2 and Z are defined as indicated above.

11. A chiral diphosphine-diborane compound of the formula



in which R^1 and R^2 are defined as indicated in claim 1 and Z is $CH_2-SiR_2-CH_2$, where R is C_1-C_4 -alkyl, C_5-C_6 -cycloalkyl, C_6-C_{10} -aryl, benzyl or phenethyl.

12. A chiral diphosphine-diborane compound according to claim 11 which is selected from the group consisting of

(R,R)-bis[(o-anisylphenylphosphino)methyl]diethylsilyl-
diborane,

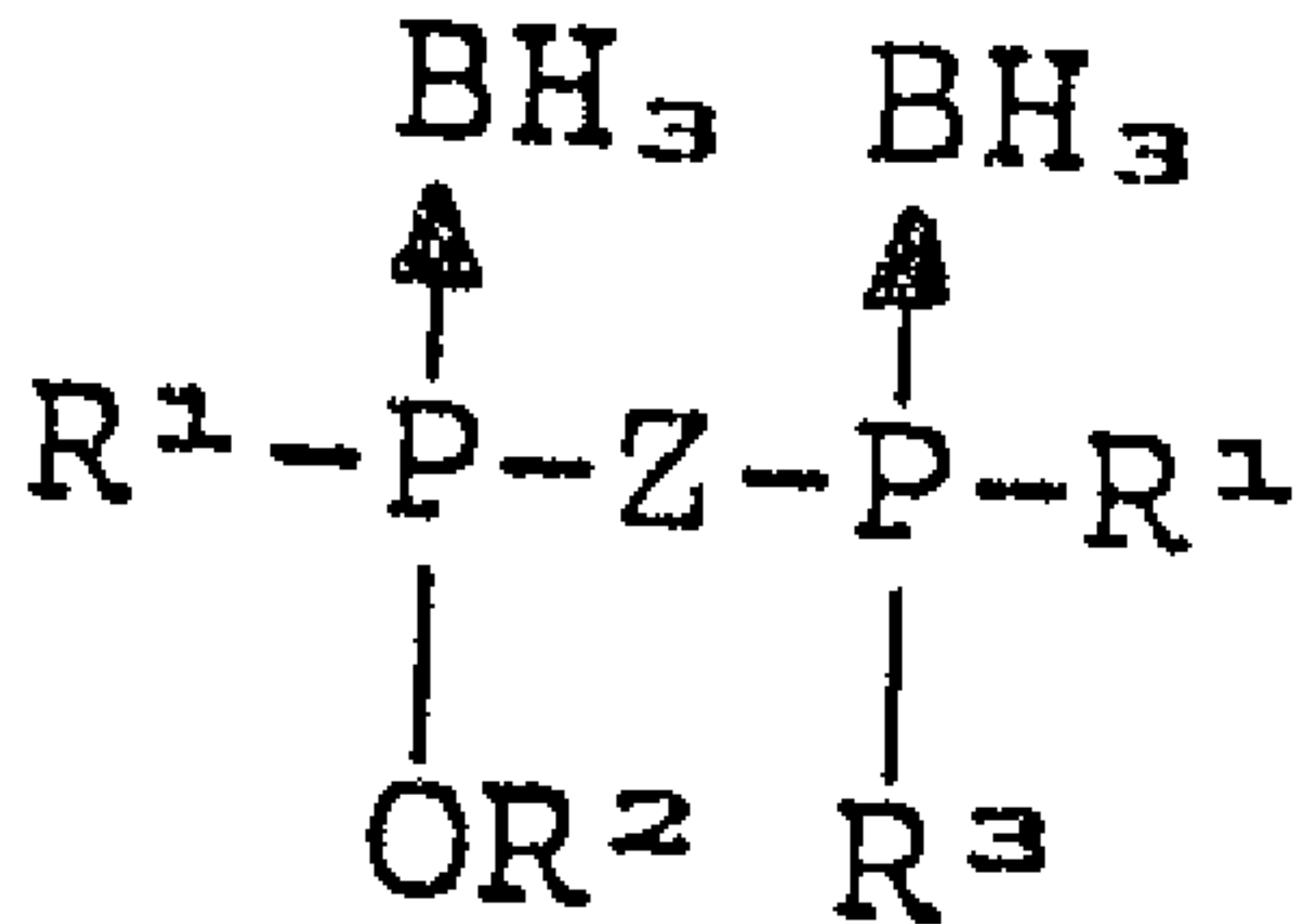
(S,S)-bis[(o-anisylphenylphosphino)methyl]diethylsilyl-
diborane,

(R,R)-bis[(2,4-dimethoxyphenylphenylphosphino)methyl]-
diphenylsilyl-diborane,

(R,R)-bis[(o-anisylphenylphosphino)methyl]diphenylsilyl-diborane,

(S,S)-bis[(o-anisylphenylphosphino)methyl]dimethylsilyl-diborane and

(S,S)-bis[(2-naphthylphenylphosphino)methyl]diphenylsilyl-diborane.



(I₀)