

Totally diastereoselective synthesis of new P-chirogenic *o*-trimethylsiloxyaryl diazaphospholidines and *o*-hydroxyaryl diazaphospholidine–borane complexes

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Dedicated to Professor François Mathey on the occasion of his 60th birthday

Abstract

The totally diastereoselective synthesis of several P(III)-chirogenic *o*-trimethylsiloxyaryl diazaphospholidines **4** was achieved by exchange reactions in refluxing toluene from the key intermediates, *o*-trimethylsiloxyaryl bis(dimethylamino) phosphines **2**, and various chiral diamines **3**. In the case of the use of a non- C_2 -symmetric chiral auxiliary such as (*S*)-2-anilinomethylpyrrolidine (**3a**), compounds **4a–g**, containing a stereogenic phosphorus atom, were obtained in diastereomerically pure form as the thermodynamic *anti*-diastereomers. Complexation of the diazaphospholidines **4** by borane-dimethylsulfide and subsequent methanolysis of the siloxy ether function lead to the formation of the desired *o*-hydroxyaryl diazaphospholidine-borane complexes **5** in good yields, ranging from 71 to 86%. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hemilabile ligands; Bidentate P–O ligands; P-stereogenic *o*-phosphinophenols; Phosphine–borane complexes; Intramolecular 1,3-carbanionic rearrangement

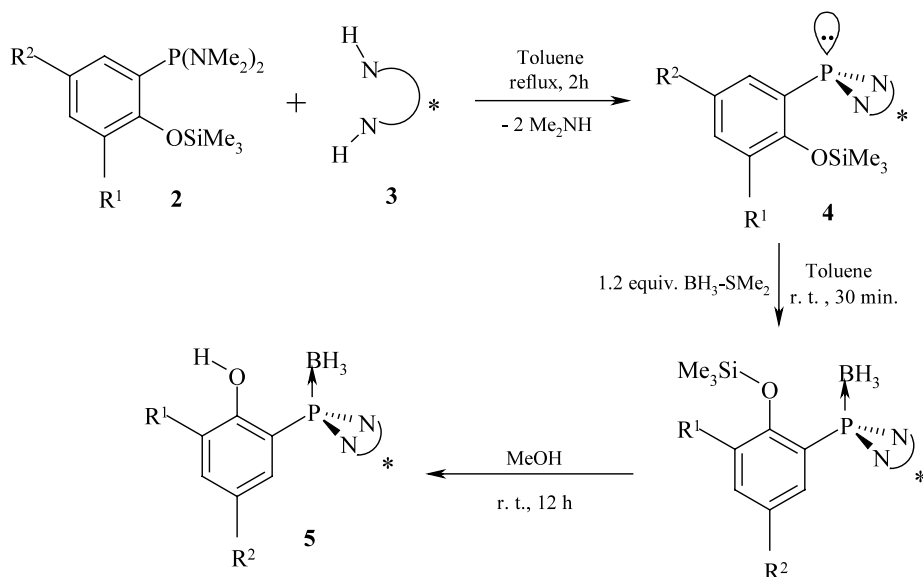
1. Introduction

Multidentate chelate ligands, offering a selection of hard-soft donor atoms that are capable of adapting to the character of the metal center, are increasingly important in organometallic chemistry [1]. In this area, hemilabile P–O ligands have been extensively studied in coordination chemistry [2], and have found applications in important catalytic processes such as oligomerization of olefins [3,4], carbonylation [5] and carbon dioxide activation [6], hydrogenation [7] or dehydrogenation [8]. Among them, *o*-phosphinophenols are ambident molecules which possess two different nucleophilic sites, a hard oxygen atom and a soft phosphorus atom. They may undergo reactions either at oxygen, phosphorus or both nucleophilic sites and, thus, are of interest in catalysis [9] and in complex chemistry [10]. Their elec-

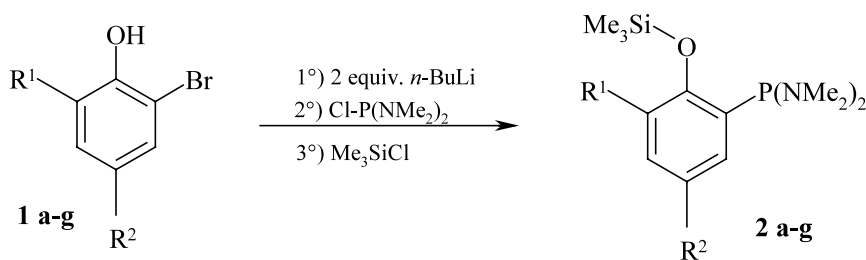
tronic and steric properties may be modulated by varying substituents at the phosphorus atom and on the aromatic ring. Until now, only few synthetic approaches to *o*-phosphinophenols have been developed. These compounds can be obtained by deprotection of suitable *o*-phosphinoaryl ethers or trimethylsilyl ethers, which in turn were synthesized from *o*-lithiated aryl ethers and diphenylchlorophosphine [10a,10b,11]. They can also be prepared via intramolecular 1,3-carbanionic rearrangement of *o*-metallated phenoxyphosphorus compounds [12]. Another general way consists in trapping of a C,O-phenol dilithium reagent with a chlorophosphine [13]. Recently, the first asymmetric synthesis of P-stereogenic 2-hydroxyarylphosphine ligands, using borane complexation methodology, and based on an intramolecular *ortho* Fries-like rearrangement mediated in basic conditions of enantioenriched *o*-bromoarylphosphinite boranes, was reported [14]. Nevertheless, only one *o*-hydroxyaryl phosphine borane complex could be obtained in pure enantiomeric form by this method. In this paper, we wish to report a

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Scheme 1. General procedure for the synthesis of the *o*-hydroxyaryl diazaphospholidine-borane complexes **5**.



Scheme 2. Synthesis of the key intermediates, *o*-trimethylsiloxyaryl bis(dimethylamino) phosphines **2**.

totally diastereoselective synthesis of new P(III)-chirogenic *o*-trimethylsiloxyaryl diazaphospholidines and *o*-hydroxyaryl diazaphospholidines, using their borane-complex form [15], according to the following general procedure (Scheme 1). Synthesis of the chiral complexes **5** may be achieved in three steps from *o*-trimethylsiloxyaryl diazaphospholidines **4**, prepared by exchange reaction in refluxing toluene from the key intermediates, *o*-trimethylsiloxyaryl bis(dimethylamino) phosphines **2** and various chiral diamines **3**. Complexation of diazaphospholidines **4** by borane-dimethylsulfide and subsequent methanolysis of the siloxy ether function may lead to the formation of the desired complexes **5**.

2. Results and discussion

2.1. Synthesis of the key intermediates, *o*-trimethylsiloxyaryl bis(dimethylamino) phosphines (**2**)

The key intermediates **2a–g** were easily prepared as described in the literature [13a,13b]. Treatment of the *o*-bromophenols **1a–g** with two equivalents of *n*-butyl-

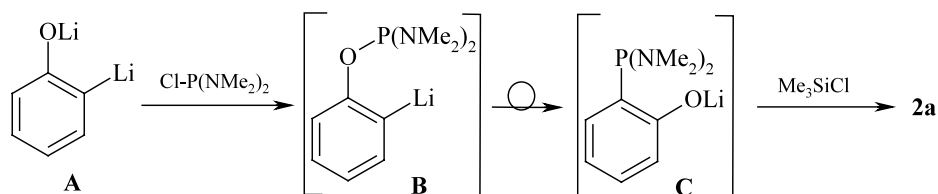
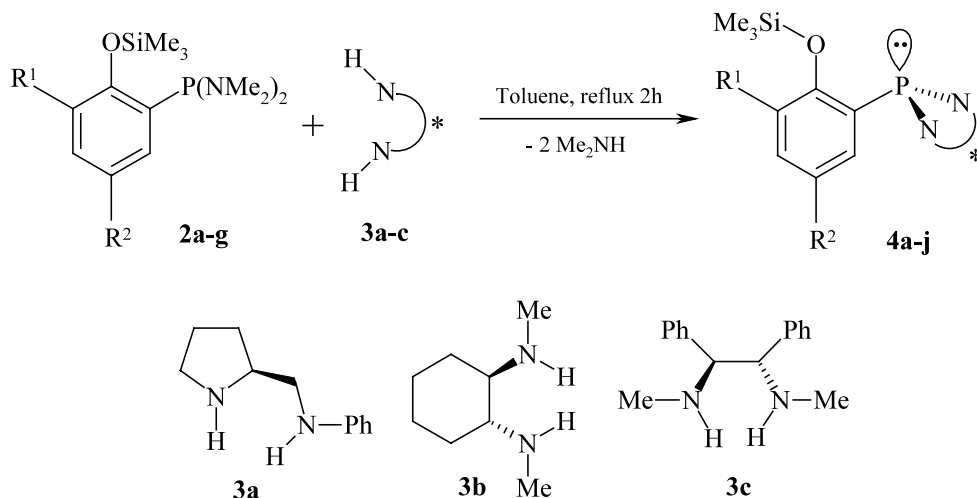
lithium lead to the formation of the corresponding C,O-dilithio reagents, which can react with one equivalent of chlorobis(dimethylamino)phosphine, affording the expected phosphinophenolate derivatives. Subsequent reaction with chlorotrimethylsilane gives the silyl ethers **2a–g** in moderate to good yields (Scheme 2 and Table 1).

In order to explain the selective C-phosphinylation of these C,O-dilithio reagents, the reaction with 2-bromophenol (entry 1) was monitored by ³¹P-NMR spec-

Table 1
Synthesis of the key intermediates, *o*-trimethylsiloxyaryl bis(dimethylamino) phosphines **2a–g**

Entry	R ¹	R ²	Product (yield ^a)
1	H	H	2a (50%)
2	H	Methyl	2b (42%)
3	H	Phenyl	2c (47%)
4	H	Cl	2d (42%)
5	Methyl	H	2e (58%)
6	<i>t</i> -Butyl	H	2f (57%)
7	<i>t</i> -Butyl	<i>t</i> -Butyl	2g (60%)

^a Isolated yield after purification by distillation.

Scheme 3. Proposed mechanism for the formation of compound **2a**.Scheme 4. Synthesis of the *o*-trimethylsiloxyaryl diazaphospholidines **4**.

troscopy. Analysis of the reaction mixture just at the end of the addition of the chlorophosphine revealed the presence of only one organophosphorus compound, with a δ_p value of 134.3 ppm. After 2 h at ambient temperature, a second compound appeared in the reaction mixture, with $\delta^{31}\text{P}$ 99.6 ppm. The reaction was complete after about 12 h. These observations led us to propose the following mechanism for the formation of precursors **2a–g** (Scheme 3). The C,O-dilithio compound **A** produced from 2-bromophenol and two equivalents of *n*-butyllithium, reacts, with one equivalent of chlorophosphine, preferably at the oxygen atom, to give the organophosphorus compound **B**. The presence of a P–O bond in compound **B** is in accordance with $\delta^{31}\text{P}$ value. A subsequent intramolecular 1,3-carbanionic P–O to P–C rearrangement is then observed leading to the formation of phenolate **C**, which can be transformed to the silyl ether **2a** by quenching the reaction with trimethylchlorosilane.

2.2. Synthesis of the *o*-trimethylsiloxyaryl diazaphospholidines (**4**)

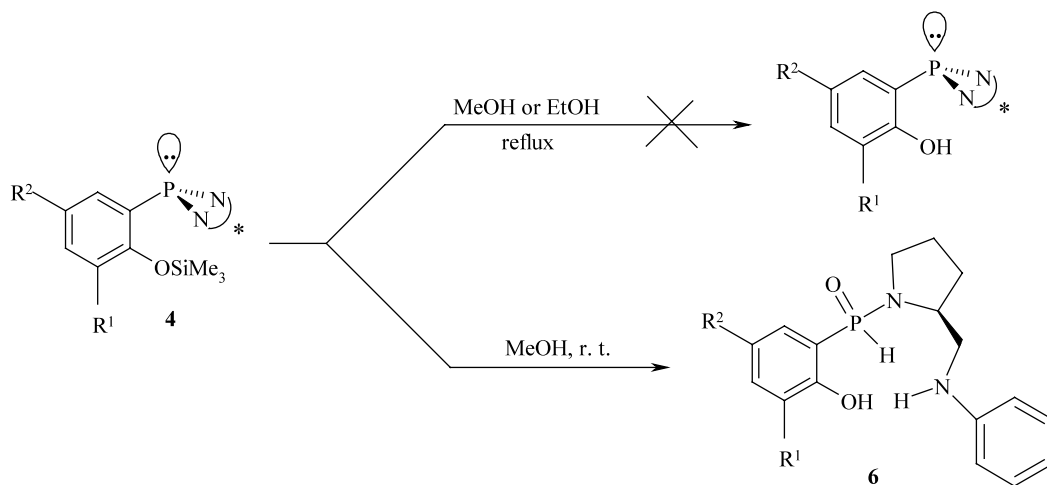
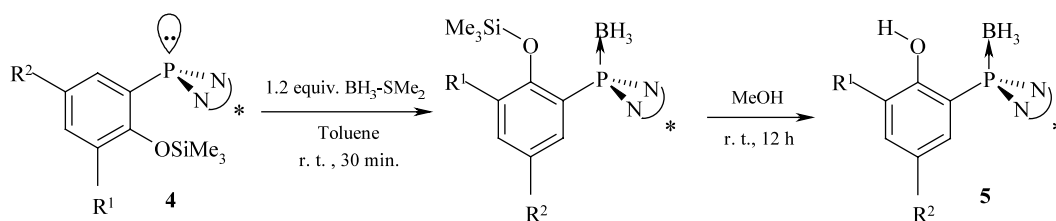
Compounds **4a–j** were readily available, from the exchange reaction in refluxing toluene between the precursors **2a–g** and various chiral diamines such as (*S*)-2-anilinomethylpyrrolidine (**3a**) [16], *N,N'*-dimethyl (1*R*,2*R*)-cyclohexanediamine (**3b**) [17] and *N,N'*-

dimethyl (1*S*,2*S*)-diphenylethanedi-amine (**3c**) [18], with moderate to high isolated yields varying from 43 to 86% (Scheme 4 and Table 2). In the case of the use of non-*C*₂-symmetric chiral auxiliaries (entries 8–14), compounds **4a–g**, containing a stereogenic phosphorus atom, were obtained in diastereomerically pure form as the thermodynamic *anti*-diastereomer. All these P(III)-chirogenic compounds were purified by distillation and are quite stable to air and moisture. They represent a new class of chiral bidentate P–O ligands which could be of great interest in coordination chemistry [1,19].

Table 2
Synthesis of the *o*-trimethylsiloxyaryl diazaphospholidines **4a–j**

Entry	<i>R</i> ¹	<i>R</i> ²	Diamine	Product (% yield ^a)
8	H	H	3a	4a (80)
9	H	Methyl	3a	4b (80)
10	H	Phenyl	3a	4c (58)
11	H	Cl	3a	4d (78)
12	methyl	H	3a	4e (68)
13	<i>t</i> -Butyl	H	3a	4f (82)
14	<i>t</i> -Butyl	<i>t</i> -Butyl	3a	4g (86)
15	H	H	3b	4h (50)
16	Me	H	3b	4i (60)
14	H	H	3c	4j (43)

^a Isolated yield after purification by distillation.

Scheme 5. Methanolysis of the silyl ether function in diazaphospholindines **4**.Scheme 6. Synthesis of the *o*-hydroxyaryl diazaphospholidine–borane complexes **5**.

2.3. Synthesis of the *o*-hydroxyaryl diazaphospholidine–borane complexes (**5**)

On the basis of Heinicke's published results [13a,13b], methanolysis of the silyl ether function in diazaphospholindines **4** may lead to the formation of the corresponding free phosphanylphenols. Unfortunately, all attempts to cleave these ethers by gentle heating with an excess of absolute ethanol or methanol gave complex mixtures of unidentified organophosphorous compounds. However, when the methanolysis was conducted at ambient temperature, formation of a major product was observed, which was not the expected free phosphanylphenol but the oxide **6** (Scheme 5). Experiments are still in progress to determine the mechanism of this reaction [20].

To bypass this problem, we decided to protect the phosphine moiety before the methanolysis reaction, using borane complex methodology. Thus, the diazaphospholindines **4a–j** react with 1.2 equivalent of $\text{BH}_3\cdot\text{SMe}_2$ in toluene for 30 min at ambient temperature, affording quantitatively the corresponding phosphine–borane complexes after evaporation of the solvent. Suspensions of these crude products in absolute methanol are then stirred at ambient temperature until complete dissolution of the solids (Scheme 6 and Table 3). After purification by chromatography on silica-gel, the expected *o*-hydroxyaryl diazaphospholidine–borane

complexes are obtained in diastereomerically pure form, and in good yields ranging from 71 to 86% (entries 15–19 and 24). However, methanolysis is not so effective in the case of the use of diazaphospholindines derived from *N,N'*-dimethyl (1*R*,2*R*)-cyclohexanediamine (entries 22 and 23), or when a substituent is present in *ortho* position on the phenol moiety (entries 20 and 21). Mixtures containing only small amounts of the desired product were obtained, due to the formation of other uncharacterised organophosphorus compounds.

Table 3
Synthesis of the *o*-hydroxyaryl diazaphospholindines **5a–h**

Entry	R^1	R^2	Precursor	Product (% yield ^a)
15	H	H	4a	5a (86)
16	H	Methyl	4b	5b (71)
17	H	Phenyl	4c	5c (76)
18	H	Cl	4d	5d (76)
19	Methyl	H	4e	5e (76)
20	<i>t</i> -Butyl	H	4f	^b
21	<i>t</i> -Butyl	<i>t</i> -Butyl	4g	^b
22	H	H	4h	5h (45)
23	Me	H	4i	5i (38)
24	H	H	4j	5j (75)

^a Isolated yield after purification by column chromatography.

^b Numerous unidentified products, but no traces of the expected free phosphinophenol.

3. Conclusion

In summary, we have developed a simple and highly diastereoselective approach for the preparation of new P(III)-chirogenic *o*-trimethylsiloxyaryl diazaphospholidines. These compounds represent a new class of chiral bidentate P–O ligands which could be of great interest in coordination chemistry. Moreover, through reaction with borane–dimethylsulfide and subsequent cleavage of the silyl ethers, they are good precursors for the synthesis of *o*-hydroxyaryl diazaphospholidines, in the form of their borane complexes. To our knowledge, this methodology represents the first accurate and totally diastereoselective synthesis of P-stereogenic 2-hydroxyarylphosphine ligands. We are currently extending the synthesis of such ligands using diols and aminoalcohols as chiral auxiliaries. Investigations of their catalytic ability as ligands or non-metallic catalysts in enantioselective processes are still in progress.

4. Experimental

4.1. General considerations

4.1.1. General

All reactions are conducted under dry argon using Schlenk technique. Diethyl ether and tetrahydrofuran (THF) were dried and freshly distilled over sodium wire. Toluene was dried and freshly distilled over calcium hydride. Methanol was dried and freshly distilled over magnesium. The purity of all reagents was checked by NMR spectroscopy. All melting points were taken on a Büchi apparatus, and are uncorrected. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ solution at 200.00 and 50.30 MHz on a Bruker AC200 spectrometer; ³¹P-NMR spectra were recorded in CDCl₃ solution at 40.50 MHz on a Bruker AC100 spectrometer (the usual abbreviations are used: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet). The chemical shift values are given in ppm, and were determined, relative to Me₄Si (¹H), CDCl₃ (¹³C), and 85% H₃PO₄ (³¹P). IR spectra were recorded on a Perkin–Elmer 298 IR spectrometer. Optical rotations were determined on a Perkin–Elmer 241 MC polarimeter.

4.2. Synthesis of the substituted *o*-bromophenols

2-Bromo-4-chlorophenol (**1d**) was purchased from Acros Organics. The method of Pearson [21] was used to prepare from the corresponding phenols, the substituted *o*-bromophenols **1a–c** and **1e–g**, which were not commercially available. Products were purified by chromatography on silica-gel.

4.2.1. 2-Bromophenol (**1a**)

Yield: 62%; colourless oil; *R*_f = 0.8 (petroleum ether); ¹H-NMR δ 7.6–6.5 (m, 4H), 5.4 (s, 1H); ¹³C-NMR δ 152.1, 129.1, 116.1, 131.9, 121.7, 110.1.

4.2.2. 2-Bromo-4-methylphenol (**1b**)

Yield: 65%; colourless oil; *R*_f = 0.9 (ethyl acetate–petroleum ether, 20:80); ¹H-NMR δ 7.3 (m, 1H), 7.1–6.9 (m, 2H), 5.7 (s, 1H), 2.3 (s, 3H); ¹³C-NMR δ 149.8, 132.0, 131.2, 129.5, 115.7, 109.6, 19.9.

4.2.3. 3-Bromo-4-hydroxybiphenyl (**1c**)

Yield: 65%; white solid; m.p. 95 °C; *R*_f = 0.9 (petroleum ether); ¹H-NMR δ 7.9–7.0 (m, 8H), 5.9 (s, 1H); ¹³C-NMR δ 151.6, 139.3, 135.3, 130.4, 128.8, 127.9, 127.2, 126.7, 116.3, 110.6.

4.2.4. 2-Bromo-6-methylphenol (**1e**)

Yield: 58%; colourless oil; *R*_f = 0.8 (petroleum ether); ¹H-NMR δ 7.2–7.1 (m, 1H), 6.9–6.8 (m, 1H), 6.6–6.4 (m, 1H), 5.3 (s, 1H), 2.2 (s, 3H); ¹³C-NMR δ 150.3, 130.3, 129.3, 125.9, 121.1, 110.1, 16.5.

4.2.5. 2-Bromo-6-tert-butylphenol (**1f**)

Yield: 60%; colourless oil; *R*_f = 0.7 (petroleum ether); ¹H-NMR δ 7.2–6.4 (m, 3H), 5.6 (s, 1H), 1.2 (s, 9H); ¹³C-NMR δ 150.4, 137.6, 129.6, 126.5, 120.9, 112.3, 35.3, 29.3.

4.2.6. 2-Bromo-4,6-ditert-butylphenol (**1g**)

Yield: 59%; white solid; m.p. 56 °C; *R*_f = 0.8 (petroleum ether); ¹H-NMR δ 7.2–6.9 (m, 2H), 5.4 (s, 1H), 1.2 (s, 9H), 1.1 (s, 9H); ¹³C-NMR δ 148.1, 143.7, 136.8, 126.4, 123.7, 112.0, 35.7, 34.5, 31.6, 29.6.

4.3. Synthesis of chlorobis(dimethylamino)phosphine

Chlorobis(dimethylamino)phosphine was prepared according to a procedure described in the literature [22]. One equivalent of PCl₃ was added dropwise at 0 °C to two equivalents of P(NMe₂)₃. The mixture was warmed to 100 °C and stirred for 1 h, the formation of the product was monitored by ³¹P-NMR spectroscopy. The product was not purified and used directly in the next step. ³¹P-NMR δ 161.9.

4.4. General procedure for the synthesis of the *o*-trimethylsiloxyaryl bis(dimethylamino) phosphines (**2a–g**)

A solution of *o*-bromophenol **1** in dry ether was cooled to –78 °C. Two equivalents of *n*-butyllithium (10 M solution in *n*-hexane) were added dropwise with stirring. The reaction mixture was then allowed to warm slowly to room temperature (r.t.) and stirring was continued for 4 h. The generated *o*-lithiophenolate

precipitated. The mixture was cooled to $-78\text{ }^{\circ}\text{C}$ and a slight excess (1.1 equivalents) of pure chlorobis(dimethylamino)phosphine was added dropwise. Stirring was continued overnight at r.t. to complete the formation of the phosphine. Subsequently, 1.2 equivalents of Me_3SiCl were added dropwise at r.t. and the mixture was stirred at least for 1 h. The precipitate was filtered and washed several times with dry ether. The solvent was evaporated under reduced pressure and the residue distilled in vacuo.

4.4.1. 2-[Bis(dimethylamino)phosphanyl]phenyl trimethylsilyl ether (**2a**)

Yield: 50%; colourless oil; b.p. $90\text{ }^{\circ}\text{C}$ (0.05 mbar); $^1\text{H-NMR}$ δ 7.5–6.8 (m, 4H), 2.7 (d, $J = 18\text{ Hz}$, 12H), 0.3 (s, 9H); $^{13}\text{C-NMR}$ δ 156.9 (d, $J = 17\text{ Hz}$), 132.3 (d, $J = 6\text{ Hz}$), 130.9 (d, $J = 7\text{ Hz}$), 129.2, 120.9, 118.7, 41.4 (d, $J = 18\text{ Hz}$), 0.6; $^{31}\text{P-NMR}$ δ 95.5.

4.4.2. 2-[Bis(dimethylamino)phosphanyl]-4-methylphenyl trimethylsilyl ether (**2b**)

Yield: 42%; colourless oil; b.p. $99\text{ }^{\circ}\text{C}$ (0.005 mbar); $^1\text{H-NMR}$ δ 7.4–6.6 (m, 3H), 2.6 (d, $J = 18\text{ Hz}$, 12H), 2.3 (s, 3H), 0.2 (d, $J = 3\text{ Hz}$, 9H); $^{13}\text{C-NMR}$ δ 154.6 (d, $J = 17\text{ Hz}$), 132.6 (d, $J = 6\text{ Hz}$), 130.3 (d, $J = 6\text{ Hz}$), 129.9, 129.7, 119.1, 41.7 (d, $J = 18\text{ Hz}$), 20.9, 0.6 (d, $J = 3\text{ Hz}$); $^{31}\text{P-NMR}$ δ 96.0.

4.4.3. 2-[Bis(dimethylamino)phosphanyl]-4-phenylphenyl trimethylsilyl ether (**2c**)

Yield: 47%; colourless oil; b.p. $150\text{ }^{\circ}\text{C}$ (0.015 mbar); $^1\text{H-NMR}$ δ 7.6–7.1 (m, 6H), 6.8–6.7 (m, 2H), 2.7 (d, $J = 18\text{ Hz}$, 12H), 0.2 (d, $J = 2\text{ Hz}$, 9H); $^{13}\text{C-NMR}$ δ 156.3 (d, $J = 16\text{ Hz}$), 141.0 (d, $J = 10\text{ Hz}$), 134.2 (d, $J = 20\text{ Hz}$), 130.9 (d, $J = 2\text{ Hz}$), 130.8 (d, $J = 3\text{ Hz}$), 128.4, 127.9, 127.7, 126.5, 126.3 (d, $J = 6\text{ Hz}$), 120.1, 118.8, 41.4 (d, $J = 18\text{ Hz}$), 0.5 (d, $J = 2\text{ Hz}$); $^{31}\text{P-NMR}$ δ 95.4.

4.4.4. 2-[Bis(dimethylamino)phosphanyl]-4-chlorophenyl trimethylsilyl ether (**2d**)

Yield: 42%; colourless oil; b.p. $138\text{ }^{\circ}\text{C}$ (0.002 mbar). $^1\text{H-NMR}$ δ 7.3–6.6 (m, 3H), 2.7 (d, $J = 18\text{ Hz}$, 12H), 0.3 (d, $J = 2\text{ Hz}$, 9H); $^{13}\text{C-NMR}$ δ 155.3 (d, $J = 17\text{ Hz}$), 133.3 (d, $J = 11\text{ Hz}$), 131.9 (d, $J = 6\text{ Hz}$), 128.8, 126.2, 119.9, 41.5 (d, $J = 18\text{ Hz}$), 0.5 (d, $J = 3\text{ Hz}$); $^{31}\text{P-NMR}$ δ 94.3.

4.4.5. 2-[Bis(dimethylamino)phosphanyl]-6-methylphenyl trimethylsilyl ether (**2e**)

Yield: 58%; colourless oil; b.p. $100\text{ }^{\circ}\text{C}$ (0.015 mbar); $^1\text{H-NMR}$ δ 7.2–6.8 (m, 3H), 2.6 (d, $J = 18\text{ Hz}$, 12H), 2.2 (s, 3H), 0.2 (d, $J = 3\text{ Hz}$, 9H); $^{13}\text{C-NMR}$ δ 155.6 (d, $J = 17\text{ Hz}$), 131.5 (d, $J = 6\text{ Hz}$), 131.3, 129.7 (d, $J = 6\text{ Hz}$), 128.9, 121.2, 40.4 (d, $J = 18\text{ Hz}$), 18.0, 1.4 (d, $J = 6\text{ Hz}$); $^{31}\text{P-NMR}$ δ 96.4.

4.4.6. 2-[Bis(dimethylamino)phosphanyl]-6-tert-butylphenyl trimethylsilyl ether (**2f**)

Yield: 57%; colourless oil; b.p. $131\text{ }^{\circ}\text{C}$ (0.02 mbar); $^1\text{H-NMR}$ δ 7.3–6.8 (m, 3H), 2.6 (d, $J = 9\text{ Hz}$, 12H), 1.3 (s, 9H), 0.3 (s, 9H); $^{13}\text{C-NMR}$ δ 155.8 (d, $J = 19\text{ Hz}$), 140.7, 132.6 (d, $J = 14\text{ Hz}$), 129.9 (d, $J = 6\text{ Hz}$), 128.0, 120.8, 41.0 (d, $J = 16\text{ Hz}$), 34.9, 30.8, 2.6 (d, $J = 10\text{ Hz}$); $^{31}\text{P-NMR}$ δ 97.4.

4.4.7. 2-[Bis(dimethylamino)phosphanyl]-4,6-di-tert-butylphenyl trimethylsilyl ether (**2g**) [13d]

Yield: 60%; colourless oil; b.p. $140\text{ }^{\circ}\text{C}$ (0.005 mbar); $^1\text{H-NMR}$ δ 7.3–7.0 (m, 2H), 2.5 (d, $J = 9\text{ Hz}$, 12H), 1.3 (s, 9H), 1.20 (s, 9H), 0.2 (s, 9H); $^{13}\text{C-NMR}$ δ 153.7 (d, $J = 18\text{ Hz}$), 139.9, 130.9 (d, $J = 15\text{ Hz}$), 127.0 (d, $J = 6\text{ Hz}$), 125.2, 124.5, 41.2 (d, $J = 15\text{ Hz}$), 35.5, 37.7, 31.2, 29.4, 2.9 (d, $J = 10\text{ Hz}$); $^{31}\text{P-NMR}$ δ 97.8.

4.5. General procedure for the synthesis of the o-trimethylsiloxyaryl diazaphospholidines **4a–g**

To a solution of **2** in dry toluene was added one equivalent of a solution of the chiral diamine **3**. The mixture was refluxed for 2 h. The solvent was then removed by evaporation under reduced pressure and the residue distilled in vacuo.

4.5.1. (2*S*,5*S*)-2-(2-Trimethylsiloxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**4a**)

Yield: 80%; yellow viscous oil; b.p. $200\text{ }^{\circ}\text{C}$ (0.005 mbar); $[\alpha]_{\text{D}}^{20} = -398$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.3–7.0 (m, 4H), 6.9–6.6 (m, 5H), 4.0–3.9 (m, 1H), 3.6 (t, $J = 7\text{ Hz}$, 1H), 3.5–3.3 (m, 1H), 3.2–3.0 (m, 2H), 2.1–1.7 (m, 4H), 0.4 (s, 9H); $^{13}\text{C-NMR}$ δ 157.6 (d, $J = 19\text{ Hz}$), 147.2 (d, $J = 14\text{ Hz}$), 132.1 (d, $J = 21\text{ Hz}$), 130.3 (d, $J = 2\text{ Hz}$), 129.0, 121.1, 119.2, 117.5 (d, $J = 13\text{ Hz}$), 116.2, 115.0 (d, $J = 4\text{ Hz}$), 64.0 (d, $J = 9\text{ Hz}$), 53.6 (d, $J = 4\text{ Hz}$), 52.5 (d, $J = 27\text{ Hz}$), 25.6 (d, $J = 6\text{ Hz}$), 17.5 (d, $J = 2\text{ Hz}$), 0.6; $^{31}\text{P-NMR}$ δ 95.6.

4.5.2. (2*S*,5*S*)-2-(2-Trimethylsiloxy-5-methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**4b**)

Yield: 80%; yellow viscous oil; b.p. $189\text{ }^{\circ}\text{C}$ (0.01 mbar); $[\alpha]_{\text{D}}^{20} = -327$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.3–7.2 (m, 2H), 7.0–6.0 (m, 1H), 6.9–6.7 (m, 5H), 4.0–3.9 (m, 1H), 3.6–3.5 (m, 1H), 3.4–3.0 (m, 3H), 2.1 (s, 3H), 2.1–1.8 (m, 4H), 0.3 (s, 9H); $^{13}\text{C-NMR}$ δ 155.3 (d, $J = 17\text{ Hz}$), 147.4 (d, $J = 17\text{ Hz}$), 131.8 (d, $J = 20\text{ Hz}$), 130.8, 130.4, 130.3 (d, $J = 9\text{ Hz}$), 129.0, 119.0, 117.4, 115.0 (d, $J = 14\text{ Hz}$), 64.0 (d, $J = 9\text{ Hz}$), 53.6 (d, $J = 5\text{ Hz}$), 52.4 (d, $J = 30\text{ Hz}$), 30.4, 25.6 (d, $J = 8\text{ Hz}$), 20.8, 0.5; $^{31}\text{P-NMR}$ δ 96.4.

4.5.3. (2*S*,5*S*)-2-(2-Trimethylsiloxy-5-phenylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane (**4c**)

Yield: 58%; yellow viscous oil; b.p. $214\text{ }^{\circ}\text{C}$ (0.004 mbar); $[\alpha]_{\text{D}}^{20} = -328$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.6–

7.0 (m, 10H), 6.9–6.5 (m, 3H), 3.9 (m, 1H), 3.6–2.9 (m, 4H), 2.1–1.3 (m, 4H), 0.3 (s, 9H); $^{13}\text{C-NMR}$ δ 156.4 (d, $J = 18$ Hz), 148.3, 147.2 (d, $J = 15$ Hz), 141.0, 134.5, 134.0, 132.2, 129.3, 129.1 (d, $J = 2$ Hz), 128.7, 128.5, 126.7, 120.3, 117.4 (d, $J = 16$ Hz), 115.1 (d, $J = 22$ Hz), 112.9, 64.1 (d, $J = 8$ Hz), 53.7 (d, $J = 4$ Hz), 52.4 (d, $J = 30$ Hz), 30.7, 25.7 (d, $J = 6$ Hz), 0.7; $^{31}\text{P-NMR}$ δ 95.9.

4.5.4. (2*S*,5*S*)-2-(2-Trimethylsiloxy-5-chlorophenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (4d**)**

Yield: 78%; yellow viscous oil; b.p. 197 °C (0.005 mbar); $[\alpha]_{\text{D}}^{20} = -313$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.2–6.6 (m, 8H), 3.96 (m, 1H), 3.9–3.8 (m, 1H), 3.4–3.6 (m, 3H), 2.1 (m, 4H), 0.3 (s, 9H); $^{13}\text{C-NMR}$ δ 156.1 (d, $J = 18$ Hz), 147.1 (d, $J = 17$ Hz), 134.8 (d, $J = 28$ Hz), 130.1, 129.7 (d, $J = 7$ Hz), 129.1, 126.4, 120.4, 117.9, 115.2 (d, $J = 14$ Hz), 64.1 (d, $J = 9$ Hz), 53.5 (d, $J = 5$ Hz), 52.5 (d, $J = 31$ Hz), 30.5, 23.6 (d, $J = 6$ Hz), 0.5; $^{31}\text{P-NMR}$ δ 94.2.

4.5.5. (2*S*,5*S*)-2-(2-Trimethylsiloxy-3-methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (4e**)**

Yield: 68%; yellow viscous oil; b.p. 210 °C (0.02 mbar); $[\alpha]_{\text{D}}^{20} = -234$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.3–7.1 (m, 3H), 6.9–6.8 (m, 5H), 4.0–3.9 (q, $J = 7$ Hz, 1H), 3.7–3.4 (t, $J = 8$ Hz, 1H), 3.4–3.3 (m, 1H), 3.2–3.0 (m, 2H), 2.3 (s, 3H), 2.1–1.8 (m, 4H), 0.5 (d, $J = 7$ Hz, 9H); $^{13}\text{C-NMR}$ δ 156.1 (d, $J = 19$ Hz), 147.0 (d, $J = 14$ Hz), 132.4, 131.3 (d, $J = 21$ Hz), 128.9 (d, $J = 2$ Hz), 128.9, 121.3, 117.4, 114.8 (d, $J = 13$ Hz), 112.7 (d, $J = 4$ Hz), 63.9 (d, $J = 9$ Hz), 53.4 (d, $J = 4$ Hz), 52.2 (d, $J = 27$ Hz), 29.8, 25.1 (d, $J = 6$ Hz), 17.5 (d, $J = 2$ Hz), 1.2 (d, $J = 6$ Hz); $^{31}\text{P-NMR}$ δ 96.6.

4.5.6. (2*S*,5*S*)-2-(2-Trimethylsiloxy-3-*tert*-butylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (4f**)**

Yield: 82%; yellow viscous oil; b.p. 190 °C (0.02 mbar); $[\alpha]_{\text{D}}^{20} = -249$ ($c = 1.05$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.4–6.8 (m, 8H), 4.0 (m, 1H), 3.7–3.1 (m, 2H), 2.2–1.8 (m, 2H), 2.1–1.8 (m, 4H), 1.7 (s, 9H), 0.6 (d, $J = 3$ Hz, 9H); $^{13}\text{C-NMR}$ δ 156.5 (d, $J = 21$ Hz), 146.8 (d, $J = 16$ Hz), 149.7, 132.1 (d, $J = 24$ Hz), 129.1, 128.5 (d, $J = 3$ Hz), 120.9, 117.6, 115.1 (d, $J = 13$ Hz), 112.8, 63.6 (d, $J = 8$ Hz), 53.4 (d, $J = 4$ Hz), 51.9 (d, $J = 25$ Hz), 34.9, 30.7, 29.5, 25.2 (d, $J = 6$ Hz), 2.9 (d, $J = 12$ Hz); $^{31}\text{P-NMR}$ δ 96.4.

4.5.7. (2*S*,5*S*)-2-(2-Trimethylsiloxy-3,5-di-*tert*-butylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]-octane (4g**)**

Yield: 86%; yellow viscous oil; b.p. 198 °C (0.02 mbar); $[\alpha]_{\text{D}}^{20} = -254$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.3–6.9 (m, 7H), 4.1 (m, 1H), 3.9–3.7 (m, 2H), 3.3–3.1 (m, 2H), 2.2–1.9 (m, 4H), 1.2 (s, 9H), 1.1 (s, 9H), 0.2 (s, 9H); $^{13}\text{C-NMR}$ δ 156.6 (d, $J = 17$ Hz), 146.8 (d, $J = 15$

Hz), 141.6, 132.3 (d, $J = 20$ Hz), 128.9, 128.4 (d, $J = 3$ Hz), 121.2, 117.1, 115.2 (d, $J = 15$ Hz), 112.9, 63.8 (d, $J = 8$ Hz), 54.0 (d, $J = 5$ Hz), 52.2 (d, $J = 26$ Hz), 35.6, 34.5, 31.4, 30.6, 29.4, 25.3 (d, $J = 6$ Hz), 2.7 (d, $J = 10$ Hz); $^{31}\text{P-NMR}$ δ 97.8.

4.5.8. (1*R*,5*R*)-2,4-Dimethyl-3-(2-Trimethylsiloxy-phenyl)-2,4-diaza-3-phosphabicyclo[4.3.0]-nonane (4h**)**

Yield: 50%; yellow viscous oil; b.p. 189 °C (0.003 mbar); $[\alpha]_{\text{D}}^{20} = +49$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.6–6.6 (m, 4H), 2.6 (d, $J = 10$ Hz, 3H), 2.5 (d, $J = 9$ Hz, 3H), 2.3–2.2 (m, 2H), 2.2–1.6 (m, 4H), 1.5–1.2 (m, 4H), 0.4 (m, 9H); $^{13}\text{C-NMR}$ δ 157.9 (d, $J = 3$ Hz), 134.1 (d, $J = 3$ Hz), 129.9, 120.2, 118.9 (d, $J = 13$ Hz), 117.4 (d, $J = 10$ Hz), 71.1 (d, $J = 3$ Hz), 64.9 (d, $J = 4$ Hz), 31.3 (d, $J = 9$ Hz), 29.1 (d, $J = 2$ Hz), 28.4 (d, $J = 6$ Hz), 28.2 (d, $J = 6$ Hz), 24.1, 23.9, 0.3; $^{31}\text{P-NMR}$ δ 103.2.

4.5.9. (1*R*,5*R*)-2,4-Dimethyl-3-(2-trimethylsiloxy-3-methylphenyl)-2,4-diaza-3-phosphabicyclo[4.3.0]-nonane (4i**)**

Yield: 60%; yellow viscous oil; b.p. 164 °C (0.02 mbar); $[\alpha]_{\text{D}}^{20} = +119$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.6–6.7 (m, 3H), 2.7 (d, $J = 10$ Hz, 3H), 2.6 (d, $J = 9$ Hz, 3H), 2.4–2.3 (m, 2H), 2.2 (s, 3H), 2.1–1.6 (m, 4H), 1.5–1.1 (m, 4H), 0.4 (m, 9H); $^{13}\text{C-NMR}$ δ 157.9 (d, $J = 2$ Hz), 147.2 (d, $J = 8$ Hz), 136.2 (d, $J = 8$ Hz), 133.9 (d, $J = 20$ Hz), 128.5 (d, $J = 2$ Hz), 117.4 (d, $J = 4$ Hz), 69.5 (d, $J = 3$ Hz), 65.6 (d, $J = 4$ Hz), 31.9 (d, $J = 6$ Hz), 29.5 (d, $J = 2$ Hz), 29.1 (d, $J = 6$ Hz), 28.7 (d, $J = 5$ Hz), 24.5, 23.4, 16.2 (d, $J = 2$ Hz), 1.2; $^{31}\text{P-NMR}$ δ 103.6.

4.5.10. (3*S*,4*S*)-2,5-Dimethyl-1-(2-trimethylsiloxy-phenyl)-2,5-diaza-4-phospholidine (4j**)**

Yield: 43%; yellow viscous oil; b.p. 194 °C (0.008 mbar); $[\alpha]_{\text{D}}^{20} = +15.8$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 7.3–6.8 (m, 13H), 3.9–3.7 (m, 2H), 2.6 (d, $J = 15$ Hz, 3H), 2.2 (d, $J = 15$ Hz, 3H), 0.3 (s, 9H); $^{13}\text{C-NMR}$ δ 158.8 (d, $J = 20$ Hz), 139.0, 138.2 (d, $J = 5$ Hz), 132.0, 130.4, 128.5, 128.2, 122.0 (d, $J = 3$ Hz), 127.8, 127.5 (d, $J = 11$ Hz), 120.7, 118.3, 75.0 (d, $J = 10$ Hz), 32.2 (d, $J = 7$ Hz), 0.5 (d, $J = 2$ Hz); $^{31}\text{P-NMR}$ δ 107.5.

4.6. Methanolysis of the silyl ether function in compound **4f**

A suspension of compound **4f** in dry methanol is stirred overnight at r.t. The solvent is then evaporated under reduced pressure and the major product formed, i.e. oxide **6** is precipitated after the addition of petroleum ether.

6: White solid; $^1\text{H-NMR}$ δ 10.1 (s, 1H), 7.6 (d, $J = 530$ Hz, 1H), 7.3–6.5 (m, 8H), 3.5 (m, 1H), 3.3 (m, 2H), 3.1–2.8 (m, 3H), 1.9–1.5 (m, 4H), 1.4 (s, 9H);

^{13}C -NMR δ 159.5 (d, $J = 5$ Hz), 147.6, 137.2 (d, $J = 8$ Hz), 130.3, 129.4 (d, $J = 10$ Hz), 129.3, 121.1, 118.7 (d, $J = 14$ Hz), 117.8, 112.9, 59.3, 44.6 (d, $J = 13$ Hz), 35.0, 31.7, 29.4, 27.9, 23.6; ^{31}P -NMR δ 18.2.

4.7. General procedure for the synthesis of the *o*-hydroxyaryl diazaphospholidine–borane complexes **5a–g**

To a solution of the chiral phosphine **4** in dry THF is added a slight excess (1.2 equivalents) of $\text{BH}_3\text{--SM}_2$. The solution is stirred for at least 30 min at r.t. Subsequently, the solvent is evaporated under reduced pressure and the residue is suspended in dry methanol. The suspension is stirred overnight at r.t. to complete the formation of **5** which is soluble in methanol. The solvent is then evaporated under reduced pressure and the product is purified by flash chromatography on silica-gel.

4.7.1. (2*S*,5*S*)-2-(2-Hydroxyphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane–borane complex (**5a**)

Yield: 86%; white solid; m.p. 115–122 °C; $R_f = 0.3$ (ethyl acetate–petroleum ether, 20:80); $[\alpha]_{\text{D}}^{20} = -164.2$ ($c = 1$, CH_2Cl_2); ^1H -NMR δ 9.8 (s, 1H), 7.6–6.7 (m, 9H), 4.1–4.0 (m, 1H), 3.9–3.6 (m, 2H), 3.4–3.1 (m, 2H), 2.2–1.7 (m, 4H), 1.1–0.1 (m, 3H); ^{13}C -NMR δ 159.2, 142.0 (d, $J = 7$ Hz), 134.0, 132.1 (d, $J = 15$ Hz), 129.1, 122.3, 119.8 (d, $J = 19$ Hz), 118.9 (d, $J = 4$ Hz), 117.7 (d, $J = 5$ Hz), 116.5 (d, $J = 35$ Hz), 61.9 (d, $J = 3$ Hz), 52.4 (d, $J = 3$ Hz), 48.6 (d, $J = 4$ Hz), 31.7, 26.3 (d, $J = 4$ Hz); ^{31}P -NMR δ 106.5 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

4.7.2. (2*S*,5*S*)-2-(2-Hydroxy-5-methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane–borane complex (**5b**)

Yield: 71%; white solid; m.p. 70–75 °C; $R_f = 0.4$ (ethyl acetate–petroleum ether, 20:80); $[\alpha]_{\text{D}}^{20} = -90.9$ ($c = 1$, CH_2Cl_2); ^1H -NMR δ 8.9 (s, 1H), 7.1–6.2 (m, 8H), 3.9 (m, 1H), 3.7–3.4 (m, 2H), 3.4–2.9 (m, 2H), 1.9 (s, 3H), 1.9–1.4 (m, 4H), 1.3–0.5 (m, 3H); ^{13}C -NMR δ 156.7 (d, $J = 3$ Hz), 142.1 (d, $J = 7$ Hz), 134.6 (d, $J = 2$ Hz), 131.9 (d, $J = 6$ Hz), 128.9 (d, $J = 4$ Hz), 128.7 (d, $J = 8$ Hz), 121.7, 118.3 (d, $J = 4$ Hz), 117.2 (d, $J = 6$ Hz), 116.2 (d, $J = 56$ Hz), 61.7 (d, $J = 2$ Hz), 52.3 (d, $J = 3$ Hz), 41.8 (d, $J = 5$ Hz), 31.4 (d, $J = 2$ Hz), 26.0 (d, $J = 4$ Hz), 20.2; ^{31}P -NMR δ 105.6 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

4.7.3. (2*S*,5*S*)-2-(2-Hydroxy-5-phenylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane–borane complex (**5c**)

Yield: 76%; white solid; m.p. 132–134 °C; $R_f = 0.3$ (ethyl acetate–petroleum ether, 5:95); $[\alpha]_{\text{D}}^{20} = -172$ ($c = 1$, CH_2Cl_2); ^1H -NMR δ 9.9 (s, 1H), 7.9–6.7 (m, 13H), 4.2–3.9 (m, 1H), 3.9–3.5 (m, 2H), 3.5–3.1 (m, 2H), 2.4–2.6 (m, 4H), 1.5–1.1 (m, 2H), 0.9 (m, 1H); ^{13}C -NMR δ 158.6 (d, $J = 3$ Hz), 141.8 (d, $J = 7$ Hz), 139.6, 132.7, 132.4, 130.3 (d, $J = 15$ Hz), 129.2, 128.4, 122.5, 119.2, 117.9, 116.2 (d, $J = 55$ Hz), 115.7 (d, $J = 3$ Hz), 115.2, 114.7, 113.2, 60.0, 52.0, 48.8, 31.7, 26.3; ^{31}P -NMR δ 107.6 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

4.7.4. (2*S*,5*S*)-2-(2-Hydroxy-5-chlorophenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane–borane complex (**5d**)

Yield: 76%; white solid; m.p. 80–85 °C; $R_f = 0.4$ (ethyl acetate–petroleum ether, 20:80); $[\alpha]_{\text{D}}^{20} = -171.8$ (CH_2Cl_2); ^1H -NMR δ 9.2 (s, 1H), 7.4–6.7 (m, 8H), 4.2–4.0 (m, 1H), 3.9–3.5 (m, 2H), 3.4–3.0 (m, 2H), 2.2–1.7 (m, 4H), 1.2–0.1 (m, 3H); ^{13}C -NMR δ 157.7 (d, $J = 3$ Hz), 141.7 (d, $J = 10$ Hz), 133.8, 131.2 (d, $J = 15$ Hz), 129.4, 124.8 (d, $J = 15$ Hz), 122.5, 119.3 (d, $J = 5$ Hz), 118.7 (d, $J = 4$ Hz), 118.0 (d, $J = 50$ Hz), 62.0, 52.5, 48.5 (d, $J = 4$ Hz), 31.8, 26.3; ^{31}P -NMR δ 105.1 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s), 650 (m).

4.7.5. (2*S*,5*S*)-2-(2-Hydroxy-3-methylphenyl)-3-phenyl-1,3-diaza-2-phosphabicyclo[3.3.0]octane–borane complex (**5e**)

Yield: 76%; white solid; m.p. 124–126 °C; $R_f = 0.25$ (ethyl acetate–petroleum ether, 5:95); $[\alpha]_{\text{D}}^{20} = -187.5$ ($c = 1$, CH_2Cl_2); ^1H -NMR δ 9.9 (s, 1H), 7.3–6.7 (m, 8H), 3.9 (m, 1H), 3.7–3.5 (m, 2H), 3.3–3.0 (m, 2H), 2.0 (s, 3H), 2.0–1.6 (m, 5H), 1.5–0.5 (m, 2H); ^{13}C -NMR δ 157.4 (d, $J = 3$ Hz), 142.2 (d, $J = 6$ Hz), 135.0 (d, $J = 2$ Hz), 129.7 (d, $J = 15$ Hz), 129.1, 126.5 (d, $J = 5$ Hz), 122.3, 119.5 (d, $J = 12$ Hz), 118.9 (d, $J = 4$ Hz), 115.5 (d, $J = 56$ Hz), 61.9 (d, $J = 3$ Hz), 52.4, 48.6 (d, $J = 4$ Hz), 31.7 (d, $J = 3$ Hz), 26.3 (d, $J = 4$ Hz), 16.0; ^{31}P -NMR δ 107.6 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

4.7.6. (1*R*,5*R*)-2,4-Dimethyl-3-(2-hydroxyphenyl)-2,4-diaza-3-phosphabicyclo[4.3.0]nonane–borane complex (**5h**)

Yield: 45%; white solid; m.p. 97–98 °C; $R_f = 0.45$ (ethyl acetate–petroleum ether, 20:80); $[\alpha]_{\text{D}}^{20} = -35.4$

($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 10.8 (s, 1H), 7.6–6.7 (m, 4H), 2.7 (d, $J = 9$ Hz, 3H), 2.6–2.5 (m, 2H), 2.3 (d, $J = 8$ Hz, 3H), 2.2–1.8 (m, 4H), 1.4 (m, 5H), 1.0–0.1 (m, 2H); $^{13}\text{C-NMR}$ δ 160.9 (d, $J = 3$ Hz), 134.8, 134.5 (d, $J = 4$ Hz), 129.0 (d, $J = 30$ Hz), 119.8 (d, $J = 12$ Hz), 117.3 (d, $J = 4$ Hz), 67.4, 65.4 (d, $J = 3$ Hz), 31.6 (d, $J = 6$ Hz), 29.1 (d, $J = 3$ Hz), 28.7 (d, $J = 8$ Hz), 28.4 (d, $J = 6$ Hz), 24.0, 23.7; $^{31}\text{P-NMR}$ δ 116.3 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

4.7.7. (1*R*,5*R*)-2,4-Dimethyl-3-(2-hydroxy-3-methyl-phenyl)-2,4-diaza-3-phosphabicyclo[4.3.0]-nonane–borane complex (5i**)**

Yield: 38%; white solid; m.p. 122–124 °C; $R_f = 0.45$ (ethyl acetate–petroleum ether, 20:80); $[\alpha]_{\text{D}}^{20} = -52.3$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 10.3 (s, 1H), 7.9–6.9 (m, 3H), 2.5 (d, $J = 36$ Hz, 3H), 2.2 (d, $J = 21$ Hz, 3H), 1.7–1.2 (m, 6H), 1.2–1.1 (m, 4H), 1.2 (s, 3H), 1.0–0.6 (m, 3H); $^{13}\text{C-NMR}$ δ 160.9 (d, $J = 2$ Hz), 146.7 (d, $J = 8$ Hz), 137.8 (d, $J = 8$ Hz), 133.6 (d, $J = 20$ Hz), 127.9 (d, $J = 2$ Hz), 119.4 (d, $J = 4$ Hz), 68.3 (d, $J = 3$ Hz), 66.3 (d, $J = 4$ Hz), 31.7 (d, $J = 4$ Hz), 29.6 (d, $J = 2$ Hz), 29.1 (d, $J = 8$ Hz), 28.7 (d, $J = 6$ Hz), 24.5 (d, $J = 2$ Hz), 23.9 (d, $J = 2$ Hz), 16.2 (d, $J = 2$ Hz); $^{31}\text{P-NMR}$ δ 117.9 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

4.7.8. (3*S*,4*S*)-2,5-dimethyl-1-(2-hydroxyphenyl)-2,5-diaza-4-phospholidine–borane complex (5j**)**

Yield: 75%; white solid, m.p. 65–75 °C; $R_f = 0.3$ (ethyl acetate–petroleum ether, 20:80); $[\alpha]_{\text{D}}^{20} = -20.1$ ($c = 1$, CH_2Cl_2); $^1\text{H-NMR}$ δ 10.4 (s, 1H), 8.2–7.8 (m, 4H), 7.6–6.9 (m, 10H), 4.3–4.0 (m, 2H), 2.5 (d, $J = 12$ Hz, 3H), 2.2 (d, $J = 12$ Hz, 3H), 1.4–0.5 (m, 3H); $^{13}\text{C-NMR}$ δ 160.9 (d, $J = 2$ Hz), 138.4, 136.6 (d, $J = 9$ Hz), 135.3 (d, $J = 4$ Hz), 134.9, 128.9, 128.8, 128.5, 128.4, 127.9 (d, $J = 10$ Hz), 120.2, 117.4 (d, $J = 4$ Hz), 75.2 (d, $J = 3$ Hz), 31.7 (d, $J = 7$ Hz), 14.2; $^{31}\text{P-NMR}$ δ 117.5 (br); IR (neat, cm^{-1}): 3470 (s, OH), 3095 (m), 2975 (m), 2950 (m), 2883 (m), 2387 (s, BH), 2348 (m, BH), 1630 (m), 1602 (s), 1501 (s), 1310 (s), 1287 (s), 1187 (s).

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