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Highly Enantiomerically Enriched Chlorophosphine Boranes: Synthesis and Applications as P-Chirogenic Electrophilic Blocks

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The stereoselective synthesis of P-chirogenic chlorophosphine boranes **4** was investigated by HCl acidolysis of the corresponding aminophosphine boranes **10**. The reaction afforded the P−N bond cleavage with inversion of the configuration at the phosphorus center, leading to the chlorophosphine boranes **4** with high to excellent enantiomeric purities (80−99% ee), except in the case of the chloro-1-naphthylphenylphosphine borane **4d**. Reaction conditions and workup significantly influence the enantiomeric purity of the product, with the exception of the *o*-anisyl- and *o*-tolylchlorophenylphosphine boranes, **4b** and **4c**, which were found to be particularly stable even after purification by chromatography on silica gel. Reaction of the chlorophosphine boranes **4** with various nucleophiles, such as carbanions, phenolates, thiophenolates, or amides, afforded the corresponding organophosphorus borane complexes via P−C, P−O, P−S, and P−N bond formation, respectively, in 34−93% yield and with up to 99% ee. This work demonstrates the importance of chlorophosphine boranes **4** as new and powerful electrophilic building blocks for the highly stereoselective synthesis of P-chirogenic organophosphorus compounds.

Introduction

C_2-Symmetric diphosphines or (phosphinoaryl) oxazolines with a stereogenic carbon backbone are widely used as chiral ligands in asymmetric reactions for C−H or C−C bond formation catalyzed by transition-metal complexes.[1,2] Nevertheless, other classes of phosphorus ligands, in which the chirality comes from a planar chirality,[3] an amino alcohol,[4] or a carbohydrate,[5] could also lead to highly stereoselective catalysts. The synthesis of these ligands is usually performed with the achiral chlorophosphines **1**, either as electrophilic[6] ($R^1 = R^2$, Scheme 1a) or nucleophilic reagents,[7] through the formation, in the latter case, of the phosphides **2** (Scheme 1b).

If the enantiomerically enriched chlorophosphines **1** (Scheme 1, $R^1 \neq R^2$) could be obtained, they would be useful in the synthesis of a new classes of bulky or chelating monophosphines, hybrid or functionalized ligands, with a P-chirogenic atom. It should be pointed out that the stereoselective synthesis of P-chirogenic ligands is also of particular interest for catalysts bearing only a monophosphine[8] or to increase the number of availables stereoisomers from a designated ligand.[9]

Unfortunately, the synthesis of chiral chlorophosphine **1** proceeds with complete racemization,[10,11] and only the partially enantiomerically enriched *tert*-butylchlorophe-

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(1) (a) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis with Transition Metal Compounds, Products and Catalysis*; VCH: Basel, 1993; Vol. 1. (b) Brunner, H.; Zettlmeier, W. *Handbook of Enantioselective Catalysis with Transition Metal Compounds, Ligands-References*; VCH: Basel, 1993; Vol. 2.

(2) (a) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH: New York, 1993. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley & Sons: New York, 1994. (c) Palmer, M. J.; Wills, M. *Tetrahedron*: *Asymmetry* **1999**, *10*, 2045−2061. (d) Tenaglia, A.; Heumann, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2180−2184. (e) McCarthy, M.; Guiry, P. J. *Tetrahedron* **2001**, *57*, 3809−3844.

(3) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062−4066. (b) Togni, A.; Hayashi, T. *Ferrocenes*; VCH: Basel, 1995.

(4) (a) Agbossou, F.; Carpentier, J. F.; Hapiot, F.; Suisse, I.; Mortreux, A. *Coord. Chem. Rev.* **1998**, *178−180*, 1615−1645. (b) Devocelle, M.; Mortreux, A.; Agbossou, F.; Dormoy, J. R. *Tetrahedron Lett.* **1999**, *40*, 4551−4554.

(5) (a) Selke, R.; Ohff, M.; Riepe, A. *Tetrahedron*, **1996**, *52*, 15079−15102. (b) RajanBabu, T. V.; Radetich, B.; You, K. K.; Ayers, T. A.; Casalnuovo, A. L.; Calabrese, J. C. *J. Org. Chem.* **1999**, *64*, 3429−3447. (c) Deerenberg, S.; Pamies, O.; Dieguez, M.; Claver, C.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Org. Chem.* **2001**, *66*, 7626−7631.

(6) For selected examples of synthesis of phosphorus ligands using chlorophosphine as electrophilic blocks, see: (a) Sprinz, J.; Helmchen, G. *Tetrahedron Lett.* **1993**, *34*, 1769−1772. (b) Deaton, D. N. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: Chichester, 1995; Vol. 2. (c) See also refs 4 and 5.

(7) For a typical synthesis of phosphorus ligands using chlorophosphine as the phosphide precursor, see: Peer, M.; de Jong J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547−7583.

(8) For a pertinent review on monophosphines or derivative ligands, see: (a) Lagasse, F.; Kagan, H. B. *Chem. Pharm. Bull.* **2000**, *48* (3), 315−324. (b) Komarov, I. V., Börner, A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1197−1200.

(9) Moulin, D.; Darcel, C.; Jugé, S. *Tetrahedron*: *Asymmetry* **1999**, *10*, 4729−4743.

(10) Horner, L.; Jordan, M. *Phosphorus Sulfur* **1980**, *8*, 235−242.

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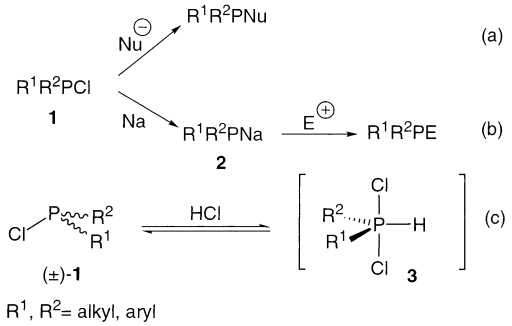
TABLE 1. Influence of Acidolysis Conditions on the Stereoselectivity

	aminophosphine borane		acidolysis conditions			phosphine borane				
entry	R^1		HCl (equiv)	[**11**] (mM)	time (h)	R^3		yields (%)	ee[a] (%)	abs config
1	Me	**11a**	6	20	24	*o*-An	**12a**		0	*R*,*S*
2	Me	**11a**	2	50	1.3	*o*-An	**12a**	82	80	*S*
3	Me	**11a**	2.1	20	1	*o*-An	**12a**	80	90	*S*
4	*o*-An	**11b**	6	60	24	Me	**12b**[b]		87	*R*
5	*o*-An	**11b**	6	60	1	Me	**12b**	75	95	*R*
6	*o*-An	**11b**	2.1	180	1	Me	**12b**	90	98	*R*
7	*o*-Tol	**11c**	6	60	1	Me	**12c**	61	98	*R*
8	1-Np	**11d**	2.1	20	1	Me	**12d**	50	0	*R*,*S*
9	2-Np	**11e**	3	130	1	Me	**12e**	46	85	*R*
10	*o*-PhPh	**11f**	6	20	1	Me	**12f**	41[c]	99	*R*
11	*c*-Hex	**11g**	6	60	3	Me	**12g**	46	80	*R*
12	*t*-But	**11h**	6	60	24					

[a] Determined by HPLC with Chiralcel OK. [b] **12a** and **12b** are enantiomers. [c] Isolated yield for 50% conversion.

SCHEME 1



nyl phosphine **1a** (R^1 = Ph, R^2 = *t*-Bu) has been described to date.[12,13] However, this compound slowly racemized in 24 h at room temperature. The racemization of the chlorophosphine can be explained by trace amounts of HCl implying reversible protonation of the phosphorus atom, with a concerted backside attack of the chlorine, resulting in the achiral pentacoordinated intermediate **3**[11] (Scheme 1c).

Complexed to the borane moiety, the chlorophosphines **4** produce stable compounds that have similar reactivity to the P^{III} derivatives (Scheme 2).[14] Since the borane complexes **5** allow the free tricoordinate phosphorus compounds **6** to retain their configuration,[15] and since these complexes can be used directly for organic[16] or coordination chemistry[17] (Scheme 2), the potentially versatile applications of P-chirogenic chlorophosphine boranes **4** were studied.

In earlier works, we reported preliminary results on the use of the chlorophosphine boranes **4** for the stereoselective synthesis of phosphorus ligands.[18a−c] Although the borane complexation confers a better configurational stability on the chlorophosphines, they must be prepared and handled with caution. This may be why there are so few applications of chiral chlorophosphine boranes in the literature.[19]

We wish to report here the stereoselective preparation of the alkyl and aryl chlorophenylphosphine boranes **4** and their reactions with various nucleophiles (Scheme 2).

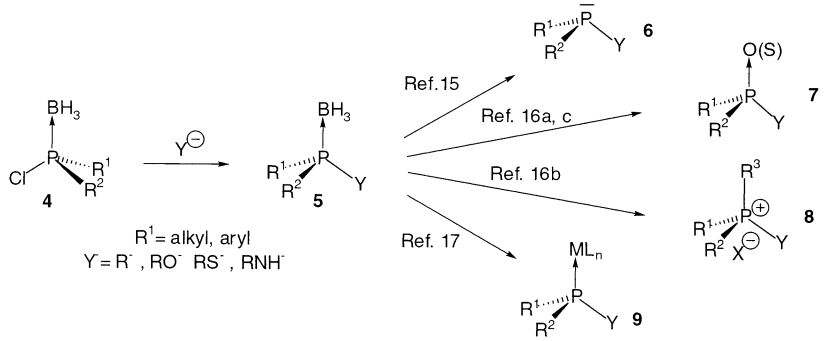
Results and Discussion

Preparation of the Chlorophosphine Boranes. Several years ago, we described[20] the diastereospecific synthesis of the aminophosphine boranes **11** by the reaction of organolithium reagents with the oxazaphospholidine borane complex **10** (Scheme 3).

Under acidic conditions, the methanolysis of compounds **11** induces the P−N bond cleavage to give the methyl phosphinite borane $R^1PhP(BH_3)OMe$ with inversion of the configuration at the phosphorus center. Consequently, we decided to investigate the acidolysis of the aminophosphine boranes **11** in various solvents in the presence of different Lewis acids or halide reagents, such as BCl_3, PCl_5, AcCl, PPh_3·HBr, or with the mixed reagents $LiCl/H_2SO_4$ and $TMSCl/^i$PrOH. In most cases, these reaction conditions led to partial conversions, racemization, or the formation of byproducts. Finally, the acidolysis of compounds **11** was realized with a toluene solution of HCl to produce the corresponding chlorophosphine boranes **4** in 41−90% isolated yields (Tables 1 and

(11) Humbel, S.; Bertrand, C.; Darcel, C.; Bauduin, C.; Jugé, S. *Inorg. Chem.* **2003**, *42*, 420−427.
(12) Omelanczuk, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1718−1719.
(13) For kinetic resolution studies of chlorophosphine **1**, see: (a) Kolodiazhnyi, O. I. *Tetrahedron* **1998**, *9*, 1279−1332. (b) Perlikowska, W. Gouygou, M.; Daran, J. C.; Balavoine, G.; Mikolajczyk, M. *Tetrahedron Lett.* **2001**, *42*, 7841−7845.
(14) (a) Schmidbaur, H. *J. Organomet. Chem.* **1980**, *200*, 287−306. (b) Yoder, C. H.; Miller, L. A. *J. Organomet. Chem.* **1982**, *228*, 31−35. (c) Knochel, P.; Langer, F.; Longeau, A.; Rottländer, M.; Stüdemann. *Chem. Ber.* **1997**, *130*, 1021−1027. (d) Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1998**, 1391−1415.
(15) (a) Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301−5303. (b) For a recent review of borane decomplexation with amines, olefins, ethanol, or acids, see ref 16c.
(16) (a) Imamoto, T.; Hirose, K.; Amano, H. *Main Group Chem.* **1996**, *1*, 331−338. (b) Uziel, J.; Riegel, N.; Aka, B.; Figuière, P.; Jugé, S. *Tetrahedron Lett.* **1997**, *38*, 3405−3408. (c) Uziel, J.; Darcel, C.; Moulin, D.; Bauduin, C.; Jugé, S. *Tetrahedron*: *Asymmetry* **2001**, *12*, 1441−1449.
(17) (a) Stéphan, O.; Riegel, N.; Jugé, S. *J. Electroanal. Chem.* **1997**, *421*, 5−8. (b) Hamada, Y.; Matsuura, F.; Oku, M.; Hatano, K.; Shioiri, T. *Tetrahedron Lett.* **1997**, *38*, 8961−8964. (c) Riegel, N.; Darcel, C.; Stéphan, O.; Jugé. S. *J. Organomet. Chem.* **1998**, *567*, 219−233. (d) Brodie, N.; Jugé, S. *Inorg. Chem.* **1998**, *37*, 2438−2442. (e) Darcel, C.; Kaloun, E. B.; Merdès, R.; Moulin, D.; Riegel, N.; Thorimbert, S.; Genêt, J. P.; Jugé, S. *J. Organomet. Chem.* **2001**, *624*, 333−343.
(18) (a) Kaloun, E. B.; Merdès, R.; Genêt, J. P.; Uziel, J.; Jugé, S. *J. Organomet. Chem.* **1997**, *529*, 455−463. (b) Moulin, D.; Darcel, C.; Jugé, S., *Tetrahedron*: *Asymmetry* **1999**, *10*, 4729−4743. (c) Moulin, D.; Bago, S.; Bauduin, C.; Darcel, C.; Jugé, S. *Tetrahedron*: *Asymmetry* **2000**, *11*, 3939−3956.
(19) (a) Schuman, M.; Trevitt, M.; Redd, A.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2000**, *39*, 2491−2493. (b) Maienza, F.; Spindler, F.; Thommen, M.; Pugin, B.; Malan, C., Mezzetti, A. *J. Org. Chem.* **2002**, *67*, 5239−5249.

SCHEME 2



SCHEME 3

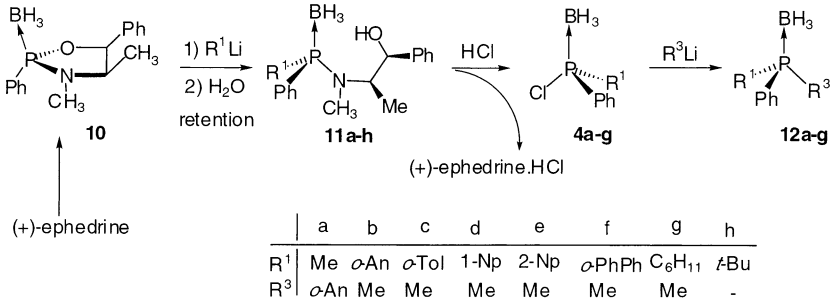


TABLE 2. Influence of Purification of the Chlorophosphine Borane 4 on Its Enantiomeric Purity

	compd **11**		chlorophosphine·BH_3 **4**					
					isolated	absolute	ee[b] (%)	
entry	R^1			aspect	yields[a] (%)	config	with purif	without purif
1	Me	**11a**	**4a**	oil	85	*R*	63	90
2	*o*-An	**11b**	**4b**	solid	99	*S*	95	98
3	*o*-Tol	**11c**	**4c**	oil	87	*S*	95	98
4	1-Np	**11d**	**4d**	oil	68	*S*	0	0
5	2-Np	**11e**	**4e**	oil	61	*S*	68	85
6	*o*-PhPh	**11f**	**4f**	solid	45	*S*	59	99
7	*c*-Hex	**11g**	**4g**	oil	74	*R*	-	80

[a] After filtration on a short column of silica gel. [b] Determined by HPLC with Chiralcel OK of the corresponding phosphine borane derivatives **12a**−**g**.

2). The enantiomeric purity of the compounds **4** was determined by HPLC on a chiral column of the corresponding phosphine boranes **12**, resulting from the reaction of **4** with an organolithium reagent (Table 1, Scheme 3).[21]

First, it should be noted that the extent of acidolysis depends on the steric hindrance of the substituents on the phosphorus atom. Thus, the chemical yields of the products decrease from methyl to biphenylaminophosphine borane (i.e., **11a**−**f**, Table 1, entries 1−10). In the case of the cyclohexyl analogues **11g**, acidolysis requires 3 h for a satisfactory yield, while no reaction was observed with the *tert*-butyl aminophosphine borane **11h** (Table 1, entries 11 and 12).

The stereoselectivity depends on the excess of HCl used. When chlorophosphine borane **4a** was formed from acidolysis of **11a** with 6 equiv of HCl, the *o*-anisylmethylphenylphosphine borane (PAMP borane) **12a** resulting from reaction with *o*-anisyllithium was obtained in racemic form (Table 1, entry 1). In the case of the acidolysis of **11a** at a concentration of 50 mM, with 2 equiv of HCl, the chlorophosphine borane **4a** leads to the (*S*)-**12a** with 80% ee (Table 1, entry 2). Finally, the (*S*)-PAMP borane **12a** was obtained with 90% ee when the acidolysis step of **11a** was carried out for 1 h at a concentration of 20 mM and in the presence of 2.1 equiv of HCl (Table 1, entry 3). The absolute configuration of the phosphine **12a** suggests that inversion of configuration occurs both in the acidolysis step and in the nucleophilic substitution of **4a**. To the best of our knowledge, that is in good agreement with the stereochemistry of the single nucleophilic displacement at P-center in acyclic phosphinous derivatives, including borane complexes.[22]

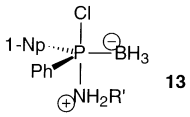
In the case of compound **11b**, the concentration and reaction time have less influence for the stereoselectivity of the acidolysis. Thus, in the presence of 6 equiv of HCl, **11b** at a concentration of 60 mM leads to the chlorophosphine **4b**, which affords the (*R*)-PAMPborane **12b** (enan-

(20) (a) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357−6360. (b) Jugé, S.; Stephan, M.; Merdès, R.; Genêt, J. P.; Halut-Desportes, S. *J. Chem. Soc., Chem. Commun.* **1993**, 531−532.

(21) The high enantiomeric excesses obtained in most cases prove the stereospecificity of the organolithium reaction with the chlorophosphine boranes **4**.

tiomer of **12a**) with 87% ee by trapping **4b** after 24 h with methyllithium (Table 1, entry 4). In addition, if the chlorophosphine borane **4b** is quenched after 1 h, or if the concentration of the starting aminophosphine borane **11b** is higher (170 mM), the (*R*)-PAMPborane **12b** is obtained with up to 98% ee (Table 1, entries 5 and 6).

Acidolysis of the *o*-tolylaminophosphine borane **11c** with 6 equiv of HCl affords **4c** and, after quenching with methyllithium, the phosphine borane **12c** with 98% ee (Table 1, entry 7). Surprisingly, the acidolysis of the 1-naphthylaminophosphine borane **11d** gives racemic products (Table 1, entry 8), whereas the 2-naphthyl analogous **11e** leads to the methyl-2-naphthylphenylphosphine borane **12e** with 85% ee (Table 1, entry 9). Although the mechanism and the origin of the racemization remain to be determined, we would suggest that the racemization of the chloro-1-naphthylphosphine borane **4d** occurs because of a particularly low energy barrier for the stereopermutation of the pentacoordinate intermediate **13**.[23]



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When the phosphine borane was prepared from acidolysis of the biphenyl aminophosphine borane **11f** in the presence of 6 equiv of HCl, for 1 h, followed by the reaction with methyllithium, compound **12f** was obtained with 99% ee (Table 1, entry 10). However, the acidolysis of **11f** was slow, and a conversion of only 50% was observed after 1 h. Finally, the acidolysis of the amino-*c*-hexylphosphine borane **11g** with HCl (3 equiv) for 3 h produced the chlorophosphine borane **4g** and then the phosphine complex **12g** with 80% ee (Table 1, entry 11). This result confirms that by increasing the reaction time, even if the conversion is higher, the enantiomeric purity of the chlorophosphine borane and its derivatives decreases.

On the other hand, the chlorophosphine boranes **4** could be readily isolated and purified. Thus, the acidolysis of the aminophosphine boranes **11a**−**g** was carried out following the conditions described in Table 1 (entries 3, 6, and 7−11). After filtration of the ephedrine hydrochloride, half of the chlorophosphine **4** was trapped by reaction with *o*-anisyl- or methyllithium to afford the corresponding phosphine borane **12**. The other half of the solution of the chlorophosphine borane **4** was quickly purified by filtration on a short column of silica gel before quenching with the organolithium reagent. In both cases, the enantiomeric purity of the phosphine borane **12** was determined by HPLC chromatography on Chiralcel OK.

The acidolysis of the aminophosphine boranes **11a**−**g** with HCl furnishes the corresponding chlorophosphine boranes **4a**−**g** in moderate to excellent isolated yields (Table 2). However, the short chromatography affords the chlorophosphine boranes **4a**, **4e**, and **4f** with 63, 68, and 59% ee, respectively, versus 85−99% ee without purification (Table 2, entries 1, 5, and 6). Nevertheless, the enantiomeric excess of the *o*-anisyl and *o*-tolyl chlorophosphine boranes, **4b** and **4c**, decreases only slightly with purification (95% ee), thus demonstrating their excellent configurational stability (Table 2, entries 2 and 3).

Finally, since the chlorophosphine boranes **4** were obtained with better stereoselectivity without purification, the excess of HCl was eliminated by several vacuum/argon cycles, after filtration of the ephedrine hydrochloride, and the toluene solution was used without further purification or storage.

Applications of the Chlorophosphine Boranes 4. The reactions of the chlorophosphine boranes **4** with various nucleophiles were investigated in order to explore their synthetic potential. The chlorophosphine boranes **4** were previously prepared in toluene solution, degassed as described above, and used without delay. The results are reported in the Table 3.

We have shown that the reaction of *o*-anisyl- or methyllithium reagent with the chlorophosphine boranes **4** (except the naphthyl derivative **4d**) furnishes the corresponding phosphine boranes **12** in good yields and with enantiomeric excesses higher than 80% (Table 2). When the chlorophosphine borane **4c** was reacted with the *o*-anisyllithium reagent, a mixture of the triarylphosphine (*R*)-**14** and its borane complex was obtained. After complete decomplexation of the mixture in ethanol at room temperature, the enantiomerically pure phosphine (*R*)-**14** was isolated in 93% yield (Table 3, entry 3). The easy decomplexation of the phosphine **14** must come from the steric crowding, which was calculated at 182° using the Tolman's cone angle concept.[24] The absolute configuration of the phosphine **14** was assigned assuming a stereochemistry with inversion during the nucleophilic substitution of **4c**, and this was in good agreement with the X-ray structure.

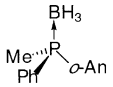
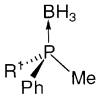
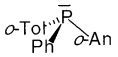
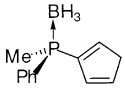
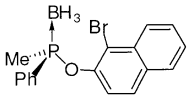
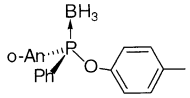
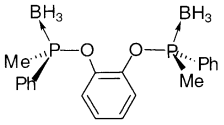
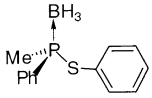
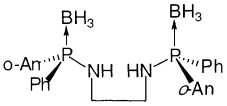
We have shown in preliminary work that the (*R*)-chlorophosphine borane **4a** produces the (*R*)-cyclopentadienylphosphine borane **15**[18a] or the (*S*)-1-bromo-2-naphthyl phosphinite borane **16**[18b] with ee up to 91%, on reaction with the cyclopentadienyl anion or the 1-bromo-2-naphthoate, respectively (Table 3, entries 4 and 5). Similarly, when the (*S*)-chlorophosphine borane **4b** reacts with the sodium *p*-cresolate, the (*R*)-*O*-*p*-tolyl phosphinite borane **17** is obtained in 85% yield and with 97% ee (Table 3, entry 6). The enantiomeric excess of **17** and its absolute configuration were established by chemical correlation to the (*S*)-PAMPborane **12a** which was prepared by reaction with methyllithium. In addition, the reaction of two equiv of (*R*)-**4a** with the lithium catecholate provides the (*S*, *S*)-diphosphinite **18** in 86% yield (Table 3, entry 7). If the enantiomeric purity has not been

(22) For pertinent reviews on the stereochemistry of single nucleophilic displacement at P-chirogenic phosphinous derivatives, see: (a) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375−1411. (b) Kolodiazhnyi, O. I. *Tetrahedron*: *Asymmetry* **1998**, *9*, 1279−1332. In the case of phosphinous borane derivatives, see: (a) ref 14c. (b) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, *178*−*180*, 665−698.

(23) Further calculations on the stereochemical pathways of the halogeno pentacoordinate intermediates **3** and analogues indicate low energy barriers (<10 kcal mol^{-1}).[11] For an example of calculations involving pentacoordinate phosphorus borane adducts, see: Solling, T. I.; Wild, S. B.; Radom, L. *J. Organomet. Chem.* **1999**, *580*, 320−327.

(24) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348. (b) The cone angle data for the tris(*o*-methoxyphenyl)phosphine (i.e., 205°) was taken from: Hirsivaara, L.; Guerricabeitia, L.; Haukka, M.; Suomalainen, P.; Laitinen, R. H.; Pakkanen, T. A.; Pursiainen, J. *Inorg. Chim. Acta* **2000**, *307*, 47−56.

TABLE 3. Reaction of Chlorophosphine Boranes 4 with Various Nucleophiles

Entry	Nucleophile	$R^1PhP(BH_3)Cl$ **4**	Product		e.e.% yields	e.e.% abs.conf.
1	*o*-AnLi	**4a**		**12a**	80	90 *S*
2	MeLi	**4b**,**c**,**4e-g**		**12b,c 12e-g**	41-90	> 80 *R*
3	*o*-AnLi	**4c**		**14**	93	99[a] *R*
4	CpNa	**4a**		**15**	83	85[b] *R*
5	1-Br-2-NpONa	**4a**		**16**	66	91[c] *S*
6	*p*-MePhONa	**4b**		**17**	85	97[d] *R*
7	*o*-Ph(OLi)$_2$	**4a**		**18**	86	- *S, S*
8	PhSLi	**4a**		**19**	87	60[e] *S*
9	$(CH_2NH)_2Na_2$	**4b**		**20**	89	96[d] *R, R*

[a] Determined by ^{31}P NMRwith a chiral palladium complex. [b] See ref 18a. [c] See ref 18c. [d] Determined by HPLC on Chiralcel OK of the PAMP borane (*S*)-**12a** (or (*R*)-**12b**). [e] Determined by HPLC on Chiralcel OK.

determined in this case, the C2 symmetric structure was proved by the X-ray analysis.

On the other hand, the reaction of the chlorophosphine (*R*)-**4a** with the lithium thiophenolate produces the thiophosphinite borane (*S*)-**19** in 87% yield and with 60% ee (Table 3, entry 8). The loss of enantiomeric purity observed here comes from the lower configurational stability of the chlorophosphine borane **4a**. Finally, (*S*)-**4b** was treated with the diamide salts, prepared from ethylenediamine, to give the diaminophosphine borane (*R*,*R*)-**20** in 89% yield and with 96% ee (Table 3, entry 9). The C_2-symmetric structure of the compound **20** was established by X-ray analysis, and its absolute configuration and enantiomeric excess were determined by correlation to the PAMP borane (*R*)-**12b**, after acidic methanolysis[25] and reaction with methyllithium.

(25) The acidic methanolysis of **20** into *o*-anisyl-*O*-methylphenylphosphinite borane was considered to proceed with inversion of configuration, as observed for various examples of aminophosphine boranes.[20]

Conclusion

In summary, we have described the stereoselective synthesis and applications of the P-chirogenic chlorophosphine boranes **4**. These compounds were prepared by P−N cleavage of the aminophosphine borane **11**, under HCl acidolysis conditions. This reaction is thought to proceed with inversion of the configuration at the phosphorus center and leads to the chlorophosphine boranes **4** with high to excellent enantiomeric purity (80−99% ee), with the exception of the chloro-1-naphthylphenylphosphine borane **4d**. A study of the acidolysis shows the importance of reaction conditions and workup on the enantiomeric purity of the product. Thus, better results were obtained when the toluene was not removed after the reaction, and when the chlorophosphine borane **4** was used immediately. However, the *o*-anisyl- and *o*-tolylchlorophosphine boranes, **4b** and **4c**, are relatively stable and can be purifed by chromatography on silica gel. Reactions of the chlorophosphine boranes **4** with various nucleophiles, such as carbanions, phenoxides, phenylthiolates, or amides, afforded the corresponding organo-

phosphorus borane complexes by P−C, P−O, P−S, and P−N bond formation, respectively, in 34−87% yields and with ee up to 99% ee.

Finally, the chlorophosphine boranes are new, useful electrophilic building blocks for the stereoselective synthesis of the P-chirogenic organophosphorus compounds.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere in dried glassware. Solvents were dried and freshly distilled under a nitrogen atmosphere over sodium/benzophenone for THF, diethyl ether, toluene, and benzene, P_2O_5 for CH_2Cl_2, calcium hydride for hexane, and sodium alcoholate for methanol, ethanol, and 2-propanol. Hexane and 2-propanol for HPLC were of chromatographic grade and used without further purification. Commercially available 2-bromoanisole and 2-bromotoluene were distilled before use, whereas 1-bromonaphthalene, 2-bromonaphthalene, 2-bromobiphenyl, and bromocyclohexane were used without purification. The toluene HCl solution was obtained by bubbling HCl gas, and the resulting solution was titrated with an indicator. Bis-dimethylaminophenylphosphine,[18a] (2*S*,4*R*,5*S*)-(−)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane **10**,[18a] and the *N*-methyl[(1*R*,2*S*)-(2-hydroxy-1-phenyl)ethyl]aminophenylphosphine boranes **11a**−**h** were prepared according to the literature.[18,20] The characteristics of the compounds **11** are reported in the Supporting Information.

HPLC analyses were performed on chromatographs equipped with UV detectors. The enantiomeric excess of the optically active derivatives was determined on Chiralcel OD and OK columns, with a hexane/^{i}PrOH mixture as the mobile phase, flow rate 1 mL·min^{-1}, and UV detection λ = 254 nm. Thin-layer chromatography was performed on silica chromagel (60 F_{254}) and visualized by UV, iodine, or permanganate treatment. Flash chromatography was performed on silica gel (60ACC, 6−35 μm and 35−70 μms). NMR spectra data were obtained on DPX 250 and Avance 300−500 spectrometers, using TMS as the internal reference for ^{1}H and ^{13}C NMR and 85% phosphoric acid as the external reference for ^{31}P NMR. Coupling constants (*J*) are reported in Hz. Melting points were measured on a Büchi 530 melting point apparatus and are uncorrected. Optical rotations values were determined at 20 °C on a 241 polarimeter. Infrared spectra were recorded on Equinox 55 and Vector 22. Mass spectral analyses were performed on R10-10C, MS 700, and Concept S at the ENSCP (Paris), ENS (Paris), and Burgundy University (Dijon), respectively. The major peak *m*/*z* is reported with the intensity as a percentage of the base peak in brackets. Elemental analyses were measured with a precision superior to 0.3% at the Microanalysis Laboratories of P. & M. Curie (Paris) and Burgundy (Dijon) Universities. The X-ray structures were determined on MACH3, CAD4, and KappaCCD diffractometers at the P. & M. Curie (Paris) and Burgundy (Dijon) Universities.

Preparation of (*R*)-(+)-Chloromethylphenylphosphine Borane 4a.[18a] In a 250 mL two-necked flask, equipped with a magnetic stirrer, an argon inlet, and a rubber septum was dissolved 0.6 g (2 mmol) of the aminophosphine borane **11a** in 89 mL of toluene. A solution of HCl in toluene (0.38 M, 11.05 mL, 4.2 mmol, 2.1 equiv) was added at room temperature under stirring, so that the final concentration of **11a** was about 20 mM. The mixture was stirred for 1 h at room temperature, and the precipitate of ephedrine hydrochloride was filtered off with a Millipore 4 μm filter. The excess of HCl was then removed by several vacuum/argon cycles, and the toluene solution of chlorophosphine borane **4a** was immediately used for synthetic applications. The analysis was carried out after purification by filtration on a short column of silica gel with toluene as eluent: yield = 85%; colorless viscous oil; R_f = 0.80 (toluene); $[\alpha]^{20}_D$ = +31.2 (*c* 2.4, $CHCl_3$), for ee = 63 ± 2%; IR (NaCl, ν cm^{-1}) 3059−2920, 2383, 1438, 1419, 1295, 1122, 1114, 1055, 911, 784, 744, 691; ^{1}H NMR ($CDCl_3$) δ (ppm) 1.20 (3H, br q, $^1J_{BH}$ = 97.0), 2.05 (3H, d, $^2J_{PH}$ = 12.9), 7.44−7.64 (3H, m), 7.82−7.88 (2H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 20.0 (d, $^1J_{PC}$ = 30.8), 129.1 (d, J_{PC} = 10.8), 130.8 (d, $^1J_{PC}$ = 45.8), 130.9 (d, J_{PC} = 12.0), 133.2 (d, J_{PC} = 2.4); ^{31}P NMR ($CDCl_3$) δ (ppm) +96.8 (q, $^1J_{BP}$ = 46.6); MS (EI) *m*/*z* (relative intensity) 160 ($M^+ - BH_3$; ^{37}Cl; 30), 158 ($M^+ - BH_3$; ^{35}Cl; 90), 153 (40), 145 ($M^+ - BH_3 - CH_3$; ^{37}Cl; 10), 143 ($M^+ - BH_3 - CH_3$; ^{35}Cl; 30), 140 (100), 123 (68), 121 (30), 107 (50), 77 (65); HRMS (EI) calcd for $C_7H_8{}^{35}ClP$ [$M^+ - BH_3$] 158.0052, found 158.0061; calcd for $C_7H_8{}^{37}ClP$ [$M^+ - BH_3$] 160.0023, found 160.0029.

The enantiomeric purity of the chloromethylphenylphosphine borane **4a** was determined by HPLC analysis on chiral column of the PAMP borane (*S*)-**12a**, resulting from reaction with *o*-anisyllithium (vide infra).

Preparation of (*S*)-(−)-*o*-Anisylchlorophenylphosphine Borane 4b.[18b] In a 50 mL two-necked flask, equipped with a magnetic stirrer, an argon inlet, and a rubber septum was introduced 2.0 mmol of the aminophosphine borane **11b**. A solution of HCl in toluene (0.38 M, 11.05 mL, 4.2 mmol, 2.1 equiv) was next added under stirring at room temperature, without previous dissolution of **11b**. After 1 h, the precipitate of ephedrine hydrochloride was filtered off with a Millipore 4 μm filter, and the excess HCl was removed by several vacuum/argon cycles. The toluene solution of **4b** was used for synthetic applications without further purification. The analysis was carried out after purification by filtration on a short column of silica gel with toluene as eluent: yield = 99%; colorless viscous oil; R_f = 0.8 (toluene); $[\alpha]^{20}_D$ = −11.1 (*c* 8.6, $CHCl_3$), for ee = 95 ± 2%; IR (NaCl, ν cm^{-1}) 3058−3010, 2941−2839, 2394, 1589, 1575, 1478, 1433, 1280, 1252, 1181, 1165, 1136, 1055, 1020, 900; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.40−2.20 (3H, m), 3.63 (3H, s), 6.91 (1H, dd, *J* = 4.6, 8.3), 7.11 (1H, td, *J* = 2.6, 7.6), 7.39−7.61 (4H, m), 7.72−7.82 (2H, m), 7.95 (1H, ddd, *J* = 1.6, 7.7, 14.9); ^{13}C NMR ($CDCl_3$) δ (ppm) 55.7, 112.0 (d, J_{PC} = 4.4), 117.6 (d, $^1J_{PC}$ = 47.7), 121.1 (d, J_{PC} = 12.3), 128.5 (d, J_{P-C} = 11.5), 128.7 (d, $^1J_{P-C}$ = 50.8), 131.1 (d, J_{P-C} = 12.9), 132.0 (d, J_{PC} = 2.6), 134.6 (d, J_{PC} = 14.3), 135.5 (d, J_{PC} = 1.8), 161.1 (d, J_{PC} = 2.4); ^{31}P NMR ($CDCl_3$) δ (ppm) +91.9 (br d, $^1J_{PB}$ = 51.4); MS (EI) *m*/*z* (relative intensity) 265 ($M - H^+$; ^{37}Cl; 3), 263 ($M - H^+$; ^{35}Cl; 9), 252 ($M^+ - BH_3$; ^{37}Cl; 33), 250 ($M^+ - BH_3$; ^{35}Cl; 100), 215 (40), 183 (35), 107 (20), 91(40), 77 (10); HRMS (EI) calcd for $C_{13}H_{12}{}^{35}ClOP$ [$M^+ - BH_3$] 250.0314, found 250.0298.

The enantiomeric purity of the *o*-anisylchlorophenylphosphine borane **4b** was determined by HPLC analysis on a chiral column of the crude PAMP borane (*R*)-**12b**, resulting from reaction with methyllithium (vide infra).

Preparation of (*S*)-(−)-Chlorophenyl-*o*-tolylphosphine Borane 4c.[18c] The preparation, use, and purification of **4c** were carried out starting from the aminophosphine borane **11c** (2 mmol) under conditions similar to those described for **4b**, using 31.6 mL of HCl solution in toluene (0.38 M, 12 mmol, 6 equiv) instead of 11.05 mL: yield = 87%; colorless viscous oil; R_f = 0.80 (toluene); $[\alpha]^{20}_D$ = −8.0 (*c* 1.05, $CHCl_3$), ee = 95 ± 5%; IR (NaCl, ν cm^{-1}) 3050−2850, 2374, 1592, 1437, 1285, 1163, 1138, 1111, 1064, 923, 807, 745, 713, 693; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.60−2.20 (3H, br), 2.32 (3H, s), 7.28−7.42 (2H, m), 7.47−7.63 (4H, m), 7.71−7.80 (2H, m), 8.02 (1H, ddd, *J* = 1.1, 7.4, 14.8); ^{13}C NMR ($CDCl_3$) δ (ppm) 21.6 (d, $^3J_{PC}$ = 4.8), 126.1 (d, J_{PC} = 12.6), 127.3 (d, $^1J_{PC}$ = 43.0), 128.9 (d, J_{PC} = 10.9), 131.0 (d, $^1J_{PC}$ = 48.9), 131.0 (d, J_{PC} = 12.3), 132.1−132.3, 133.3 (d, J_{PC} = 2.1), 134.2 (d, J_{PC} = 18.0), 142.3 (d, J_{PC} = 7.9); ^{31}P NMR ($CDCl_3$) δ (ppm) +96.7 (d, $^1J_{PB}$ = 50.6); MS (DCI, CH_4) *m*/*z* (relative intensity) 217 (68), 216 (37), 201 ($M^+ + 2H - BH_3 - Cl$; 45), 200 ($M^+ + H - BH_3 - Cl$; 100), 199 (18), 139 (9), 123 (30), 109 (29); HRMS (DCI, CH_4) calcd for $C_{13}H_{14}P$ [$M^+ + 2H - BH_3 - Cl$] 201.0833, found 201.0835. Anal. Calcd for $C_{13}H_{15}BClP$ (248.4983): C, 62.83; H, 6.08. Found: C, 62.60; H, 6.30.

The enantiomeric excess of **4c** was determined by HPLC analysis on a chiral column of the methylphenyl-*o*-tolylphos-

phine borane (*R*)-**12c**, resulting from reaction with methyllithium (vide infra).

Preparation of (±)-Chloro-1-naphthylphenylphosphine Borane 4d. The preparation, use, and purification of **4d** were carried out starting from the aminophosphine borane **11d** (2 mmol) under conditions similar to those described for **4b**, using 31.6 mL of HCl solution in toluene (0.38 M, 12 mmol, 6 equiv) and 3 h reaction time: yield = 68%; colorless viscous oil; R_f = 0.77 (toluene); IR (KBr, ν cm^{-1}) 3060−2924, 2419−2342, 1589, 1508, 1484, 1437, 1336, 1263, 1208, 1149, 1123, 1105, 1048, 1027; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.80−2.10 (3H, br), 7.40−7.63 (6H, m), 7.67−7.75 (2H, m), 7.92−7.95 (1H, m), 8.04−8.14 (2H, m), 8.27−8.37 (1H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 124.7 (d, J_{PC} = 15.0), 125.2, 126.5 (d, J_{PC} = 6.0), 126.7, 127.3, 128.6 (d, J_{PC} = 50.9), 129.0 (d, J_{PC} = 10.9), 129.5 (d, J_{PC} = 0.9), 131.2 (d, J_{PC} = 4.9), 131.1 (d, J_{PC} = 12.2), 132.3 (d, J_{PC} = 2.3), 134.0 (d, J_{PC} = 6.6), 135.0 (d, J_{PC} = 2.5), 136.0 (d, J_{PC} = 20.0); ^{31}P NMR ($CDCl_3$) δ (ppm) +94.4 (d, $^1J_{PB}$ = 45.7); MS (DCI, NH_3) *m*/*z* (relative intensity) 268 ($M^+ + H + NH_3 - Cl$; 16), 253 ($M^+ - BH_3 - Cl$; 100), 237 ($M^+ + 2H - BH_3 - Cl$; 45); HRMS (DCI, NH_3) calcd for $C_{16}H_{14}P$ [$M^+ + 2H - BH_3 - Cl$] 237.0833, found: 237.0833. Anal. Calcd for $C_{16}H_{15}BClP$ (284.5313): C, 67.54; H, 5.31. Found: C, 68.20; H, 5.68.

The racemization of the chloro-1-naphthylphenylphosphine borane **4d** was shown by HPLC analysis on a chiral column of the methyl-1-naphthylphenylphosphine borane **12d**, resulting from reaction with methyllithium (vide infra).

Preparation of (*S*)-(−)-Chloro-2-naphthylphenylphosphine Borane 4e. The preparation, use, and purification of **4e** were carried out starting from the aminophosphine borane **11e** (2 mmol) under similar conditions as described for **4b**, using 15.8 mL of HCl solution in toluene (0.38 M, 6 mmol, 3 equiv) instead of 11.05 mL: yield = 61%; colorless viscous oil; R_f = 0.83 (toluene); $[\alpha]^{20}_D$ = −7.7 (*c* 2.4, $CHCl_3$), for ee = 68 ± 2%; IR (KBr, ν cm^{-1}) 2924, 2361−2338, 1653, 1559, 1506, 1457, 1271, 1157, 1114, 1087, 953; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.80−2.30 (3H, br), 7.45−7.99 (11H, m), 8.43 (1H, d, J = 14.6); ^{13}C NMR ($CDCl_3$) δ (ppm) 126.2 (d, J_{PC} = 9.8), 127.5 (d, J_{PC} = 48.4), 127.5, 128.0, 129.0, 129.1, 129.2 (d, J_{PC} = 1.2), 129.3, 130.9 (d, J_{PC} = 48.9), 131.9 (d, J_{PC} = 12.3), 132.4 (d, J_{PC} = 3.3), 132.8 (d, J_{PC} = 2.4), 134.3 (d, J_{PC} = 15.6), 135.0 (d, J_{PC} = 2.2); ^{31}P NMR ($CDCl_3$) δ (ppm) +94.7 (d, $^1J_{PB}$ = 45.9); MS (EI) *m*/*z* (relative intensity) 272 ($M^+ - BH_3$; ^{37}Cl; 30), 270 ($M^+ - BH_3$; ^{35}Cl; 95), 236 ($M^+ + H - BH_3 - Cl$; 100), 233 ($M^+ - BH_3 - Cl$; 50), 204 (100), 158 ($M^+ - BH_3 - Ph - Cl$; 65); HRMS (EI) calcd for $C_{16}H_{12}{}^{35}ClP$ [$M^+ - BH_3$] 270.0365, found 270.0374; calcd for $C_{16}H_{12}{}^{37}ClP$ [$M^+ - BH_3$] 272.0336, found 272.0333.

The enantiomeric excess of the chloro-2-naphthylphenylphosphine borane **4e** was determined by HPLC analysis on a chiral column of the crude methyl-2-naphthylphenylphosphine borane **12e**, resulting from reaction with methyllithium (vide infra).

Preparation of (*S*)-(+)-Chloro-*o*-biphenylphenylphosphine Borane 4f. In a 250 mL two-necked flask, equipped with a magnetic stirrer, an argon inlet, and a rubber septum was introduced a solution of the aminophosphine borane **11f** (2 mmol) in dry toluene (68 mL). A solution of HCl in toluene (0.38 M, 31.6 mL, 12 mmol, 6 equiv) was then added at room temperature under stirring, making the final concentration of **11f** approximatively 20 mM. After 1 h, the ephedrine hydrochloride was filtered off with a Millipore 4 μm filter, and the excess HCl was eliminated by several vacuum/argon cycles. The toluene solution of chlorophosphine borane **4f** was used for synthetic applications without further purification. The analysis of **4f** was carried out after purification by fast chromatography on a short column of silica gel using toluene as eluent: yield = 45% (for a 50% conversion of the aminophosphine borane **11f**); colorless viscous oil; R_f = 0.77 (toluene); $[\alpha]^{20}_D$ = +12.9 (*c* 1.9, $CHCl_3$), for ee = 59 ± 2%; IR (KBr, ν cm^{-1}) 2963−2853, 2409−2344, 1462, 1436, 1384, 1261, 1127, 1105, 1086, 1052, 1026, 1008; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.70−2.10 (3H, br), 6.83−6.86 (2H, m), 7.01−7.07 (2H, m), 7.14−7.41 (7H, m), 7.45−7.63 (2H, m), 8.24−8.33 (1H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 127.4, 127.5, 128.3 (d, J_{PC} = 31.5), 128.4 (d, J_{PC} = 11.5), 129.3 (d, J_{PC} = 8.1), 129.7, 131.0 (d, J_{PC} = 12.8), 131.6 (d, J_{PC} = 2.5), 131.7, 132.1 (d, J_{PC} = 7.6), 132.4 (d, J_{PC} = 2.1), 134.0 (d, J_{PC} = 16.8), 139.3 (d, J_{PC} = 3.7), 146.9 (d, J_{PC} = 8.5); ^{31}P NMR ($CDCl_3$) δ (ppm) +97.1 (d, $^1J_{PB}$ = 40.1); MS (DCI, CH_4) *m*/*z* (relative intensity) 279 ($M^+ + 2H + CH_4 - BH_3 - Cl$; 77), 277 ($M^+ + CH_4 - BH_3 - Cl$; 100), 261 ($M^+ - BH_3 - Cl$; 15), 183 (12); MS (DCI, NH_3) *m*/*z* (relative intensity) 294 (24), 279 ($M^+ + NH_3 - BH_3 - Cl$; 95), 278 (45), 277 (100), 263 (24), 216 (8), 201 (9), 170 (13); HRMS (DCI, NH_3) calcd for $C_{18}H_{14}P$ [$M^+ - BH_3 - Cl$] 261.0833, found 261.0840. Anal. Calcd for $C_{18}H_{17}BClP$ (310.5691): C, 69.61; H, 5.52. Found: C, 70.34; H, 6.18.

The enantiomeric excess of the chloro-*o*-biphenylphenylphosphine borane **4f** was determined by HPLC analysis on a chiral column of the methyl-*o*-biphenylphenylphosphine borane **12e**, resulting from reaction with methyllithium (vide infra).

Preparation of (*R*)-(+)-Chlorocyclohexylphenylphosphine Borane 4g. The preparation, use, and purification of **4g** were carried out starting from the aminophosphine borane **11g** (2 mmol) under conditions similar to those described for **4b**, using 31.6 mL of HCl solution in toluene (0.38 M, 12 mmol, 6 equiv) and 3 h reaction time: yield = 74%; colorless viscous oil; R_f = 0.78 (toluene); $[\alpha]^{20}_D$ = +61.8 (*c* 1.8, $CHCl_3$), after purification; IR (KBr, ν cm^{-1}) 3019−2860, 2402−2347, 1451, 1438, 1216, 1056, 754, 691, 669; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.30−2.00 (3H, br), 1.10−2.25 (11H, m), 7.48−7.62 (3H, m), 7.83−7.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 25.5 (d, J_{PC} = 1.6), 25.8, 26.0 (d, J_{PC} = 1.1), 26.1 (d, J_{PC} = 1.7), 26.3 (d, J_{PC} = 2.8), 42.0 (d, $^1J_{PC}$ = 23.8), 128.7 (d, $^1J_{PC}$ = 42.8), 128.9 (d, J_{PC} = 10.7), 131.8 (d, J_{PC} = 11.3), 132.7 (d, J_{PC} = 2.6); ^{31}P NMR ($CDCl_3$) δ (ppm) +110.5 (br d, $^1J_{PB}$ = 51.0); MS (EI) *m*/*z* (relative intensity) 239 (M^+ −3H; 5), 237 ($M^+ - 3H$; 15), 228 ($M^+ - BH_3$; 40), 226 ($M^+ - BH_3$; 100), 208 (10), 191 (10), 169 (10), 145 (35), 144 (40); HRMS (EI) calcd for $C_{12}H_{16}B^{37}ClP$ [$M^+ - 3H$] 239.0746, found 239.0757; calcd for $C_{12}H_{16}B^{35}ClP$ [$M^+ - 3H$] 237.0774, found 237.0779; calcd for $C_{12}H_{16}{}^{37}ClP$ [$M^+ - BH_3$] 228.0651, found 228.0650; calcd for $C_{12}H_{16}{}^{35}ClP$ [$M^+ - BH_3$] 226.0678, found 226.0684.

The enantiomeric purity of the chlorocyclohexylphenylphosphine borane **4g** was determined from the corresponding phosphine oxide, resulting from reaction with methyllithium, then oxidation of the phosphine by the *tert*-butylhydroperoxide.[16c] The enantiomeric purity was determined by ^{1}H NMR and ^{31}P NMR analysis, using the chemical shift reagent described by Kagan [(*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylethylamine].[26]

Preparation of Tertiary Phosphine Boranes 12 from the Chlorophosphine Boranes 4. General Procedure. The organolithium reagent (2.5 equiv) is slowly added at −78 °C to the toluene solution of chlorophosphine borane **4** previously prepared. It should be noted that the enantiomer (*S*)-**12a**, which was obtained under similar conditions from **4a**, requires an excess of *o*-anisyllithium to make up for the deprotonation of the methyl substituent. The mixture is allowed to warm to room temperature then hydrolyzed with 20 mL of water. The aqueous layer is extracted twice with dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvent was evapored under reduced pressure. The residue was purified over silica gel using toluene/petroleum ether 7:3 as eluent.

The following phosphine boranes exhibit satisfactory analytical data in agreement with the literature: *o*-anisylmethylphenylphosphine boranes (*S*)-(+)-**12a** or (*R*)-(−)-**12b**,[15a,18a]

(26) Dunach, E.; Kagan, H. B. *Tetrahedron Lett.* **1985**, *26*, 2649−2652.

(*R*)-(−)-methylphenyl-*o*-tolylphosphine borane **12c**,[17e,27] (±)-methyl-1-naphthylphenylphosphine borane **12d**.[27, 28]

Their enantiomeric excesses have been determined by HPLC analysis on a Chiralcel OK Daicel column, eluent: hexane/ethanol 8:2, 1 mL/min, λ = 254 nm: (*R*)-**12b**, t_R = 11 min; (*S*)-**12a**, t_R = 21 min (**12a** is the enantiomer of **12b**); (*R*)-**12c**, t_R = 11 min; (S)-enantiomer, t_R = 15 min; (*R*)-**12d**, t_R = 21 min; (*S*)-enantiomer, t_R = 30 min.

(*R*)-(+)-Methyl-2-naphthylphenylphosphine borane 12e:[20] yield = 46%; colorless viscous oil; R_f = 0.61 (toluene); $[\alpha]^{20}_D$ = +19.0 (*c* 1.3, $CHCl_3$) for 81% ee; IR (KBr, ν cm^{-1}) 3052−2915, 2368−2337, 1437, 1089, 1068; ^1H NMR ($CDCl_3$) δ (ppm) 0.20−1.60 (3H, br), 1.82 (3H, d, $^2J_{PH}$ = 10.1), 7.10−7.90 (11H, m), 8.05−8.30 (1H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 11.9 (d, $^1J_{PC}$ = 40.2), 126.8 (d, J_{PC} = 8.6), 127.0−129.0, 130.7 (d, J_{PC} = 56.3), 131.2 (d, J_{PC} = 2.4), 131.8 (d, J_{PC} = 9.6), 132.8 (d, J_{PC} = 11.7), 133.4 (d, J_{PC} = 10.9), 134.3 (d, J_{PC} = 2.0); ^{31}P NMR ($CDCl_3$) δ (ppm) +11.7 (q, $^1J_{PB}$ = 67.5); MS (DCI, CH_4) *m*/*z* (relative intensity) 263 (M^+ − H; 100), 250 (M^+ − BH_3; 20); HRMS (DCI, CH_4) calcd for $C_{17}H_{17}BP$ [M^+ − H] 263.1161, found 263.1168.

The enantiomeric excess of the methyl-2-naphthylphenylphosphine borane **12e** was determined by HPLC analysis on a Chiralcel OK Daicel column, eluent: hexane/ethanol 8:2, 1 mL/min, λ = 254 nm: (*R*)-**12e**, t_R = 19 min; (*S*)-enantiomer, t_R = 27 min.

(*R*)-(−)-Methyl-*o*-biphenylphenylphosphine borane 12f:[29] yield = 41%; white powder; R_f = 0.70 (toluene); mp = 117 °C; $[\alpha]^{20}_D$ = −42.1 (*c* 1.0, $CHCl_3$) for 99% ee; IR (KBr, ν cm^{-1}) 2964−2854, 2391−2330, 1437, 1073, 1061, 895, 888; ^1H NMR ($CDCl_3$) δ (ppm) 0.10−1.81 (3H, br), 1.32 (3H, d, $^2J_{PH}$ = 10.1), 6.90 (2H, m), 7.10−7.60 (11H, m), 8.00 (1H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 11.8 (d, $^1J_{PC}$ = 41.0), 127.4 (d, J_{PC} = 11.6), 127.6, 128.4 (d, J_{PC} = 10.2), 128.5 (d, J_{PC} = 52.1), 129.5, 130.4 (d, J_{PC} = 2.5), 130.9 (d, J_{PC} = 2.4), 131.2 (d, J_{PC} = 9.6), 131.5 (d, J_{PC} = 6.7), 132.3 (d, J_{PC} = 57.5), 134.4 (d, J_{PC} = 15.3), 140.6 (d, J_{PC} = 3.1), 146.9 (d, J_{PC} = 3.8); ^{31}P NMR ($CDCl_3$) δ (ppm) +14.4 (q, $^1J_{PB}$ = 77.3); MS (EI) *m*/*z* (relative intensity) 290 (M^+; 15), 287 (M^+ − 3H; 20), 276 (M^+ − BH_3; 60), 275 (M^+ − BH_3 − H; 100), 183 (35), 163 (15), 123 (10); HRMS (EI) calcd for $C_{19}H_{20}BP$ [M^+] 290.1400, found 290.1396. Anal. Calcd for $C_{19}H_{20}BP$ (290.1508): C, 78.65; H, 6.95. Found: C, 78.76; H, 7.03.

The enantiomeric excess of the methyl-*o*-biphenylphenylphosphine borane **12f** was determined by HPLC analysis on a Chiralcel OK Daicel column, eluent: hexane/ethanol 70:30, 1 mL/min, λ = 254 nm: (*R*)-**12f**, t_R = 10 min; (*S*)-enantiomer, t_R = 30 min.

(*S*)-(+)-Cyclohexylmethylphenylphosphine borane 12g: yield = 46%; colorless viscous oil; R_f = 0.61 (toluene); $[\alpha]^{20}_D$ = +9.1 (*c* 1.0, $CHCl_3$) for 80% ee; IR (KBr, ν cm^{-1}) 2930−2854, 2376, 1449, 1437, 1300, 1119, 1064, 1001, 920, 898, 881, 746, 694; ^1H NMR ($CDCl_3$) δ (ppm) 0.10−1.40 (3H, br), 1.08−1.39 (6H, m), 1.53 (3H, d, $^2J_{PH}$ = 9.9), 1.57−1.94 (5H, m), 7.40−7.55 (3H, m), 7.65−7.73 (2H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 7.7 (d, $^1J_{PC}$ = 38.8), 25.8 (d, J_{PC} = 1.8), 26.3 (d, J_{PC} = 4.8), 26.4 (d, J_{PC} = 4.2), 26.6 (d, J_{PC} = 4.2), 35.8 (d, $^1J_{PC}$ = 35.8), 128.6 (d, J_{PC} = 9.7), 128.8 (d, J_{PC} = 52.1), 131.0 (d, J_{PC} = 2.4), 132.0 (d, J_{PC} = 8.5); ^{31}P NMR ($CDCl_3$) δ (ppm) +16.2 (q, $^1J_{PB}$ = 40.1); MS (DCI, CH_4) *m*/*z* (relative intensity) 236 ($M^+ + CH_4$; 25), 217 (M^+ − 3H; 75), 206 (M^+ − BH_3; 8), 171 (25), 154 (100), 136 (16), 124 (18); HRMS (DCI, CH_4) calcd for $C_{13}H_{19}BP$ [M^+ − 3H] 217.1317, found 217.1324. Anal. Calcd for $C_{13}H_{22}BP$ (220.1006): C, 70.94; H, 10.07. Found: C, 70.94; H, 10.24.

The enantiomeric excess of the cyclohexylmethylphenylphosphine borane **12g** was determined by ^1H NMR and ^{31}P NMR analysis of the crude methylcyclohexyl phenylphosphine oxide, in the presence of the (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylethylamine as the chemical shift reagent.[26] The phosphine oxide was obtained by a one-pot procedure previously described, involving decomplexation of **12g** with DABCO and then oxidation with *tert*-butyl hydroperoxide.[16c]

(*R*)-(−)-*o*-Anisylphenyl-*o*-tolylphosphine 14. The preparation of the phosphine **14** from the chlorophosphine borane **4c** was achieved as described above for the phosphine borane. However, after workup, a mixture of **14** and its borane complex (^{31}P NMR δ(ppm) 19.6, $^1J_{PB}$ = 68.5) was obtained which was taken up in ethanol and stirred overnight to complete the decomplexation: yield = 92%; white crystals (EtOH); R_f = 0.68 (toluene); mp = 134 °C; $[\alpha]^{25}_D$ = −2.88 (*c* 1.0, $CHCl_3$) for 99% ee; IR (KBr, ν cm^{-1}) 3035−2830, 1580, 1570, 1457, 1434, 1271, 1240, 1165, 1021, 794, 763, 745, 699; ^1H NMR ($CDCl_3$) δ (ppm) 2.33 (3H, s), 3.68 (3H, s), 6.53−6.58 (1H, m), 6.66−6.70 (1H, m), 6.74−6.85 (2H, m), 6.95−7.05 (1H, m), 7.08−7.30 (8H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 21.2 (d, $^3J_{PC}$ = 21.3), 55.7, 110.2 (d, J_{PC} = 1.7), 121.1, 124.7 (d, J_{PC} = 11.6, 125.9, 128.3−128.6, 129.9 (d, J_{PC} = 4.6), 130.3, 132.8, 133.7, 134.0, 134.3, 135.3−136.0, 142.3 (d, J_{PC} = 26.0), 161.3 (d, J_{PC} = 15.7); ^{31}P NMR ($CDCl_3$) δ (ppm) −23.1; MS (DCI, CH_4) *m*/*z* (relative intensity) 323 ($M^+ + H + CH_4$; 15), 307 ($M^+ + H$; 100), 215 (M^+ − *o*-Tol; 8), 199 (M^+ − *o*-An; 6); HRMS (DCI, CH_4) calcd for $C_{20}H_{20}OP$ [$M^+ + H$] 307.1252, found 307.1255.

The enantiomeric purity of **14** was analyzed by comparison with a racemic sample, by ^{31}P NMR in the presence of (+)-di-μ-chlorobis[2-[1-(dimethylamino)ethyl]phenyl-C,N]dipalladium.[30]

(*R*)-(−)-Cyclopentadienylmethylphenylphosphine Borane 15. The preparation of this compound from the chlorophosphine borane **4a** was carried out as previously described.[18a]

Preparation of the Phosphinite Boranes 16−18. (*S*)-(−)-Methyl-*O*-(1-bromo-2-naphthyl)phenylphosphinite Borane 16. The preparation of the compound **16** from the chlorophosphine borane **4a** has been previously described by our group.[18c]

(*R*)-(−)-*o*-Anisylphenyl-*O*-*p*-tolylphosphinite Borane 17. In a 50 mL two-necked flask equipped with a magnetic stirrer and an argon inlet was added 60 mg of NaH (60% in mineral oil, 1,5 mmol), and the mixture was washed several times with small amounts of dry pentane. A solution of 162 mg of *p*-cresol (1.5 mmol) in 8 mL of dry THF was then introduced, and the mixture was stirred at room temperature for 4 h. The *p*-cresolate was then added at −78 °C to a toluene solution of chlorophosphine borane **4b** (0.5 mmol) previously prepared as described above. The resulting mixture was progressively warmed to room temperature and stirred overnight. After hydrolysis, the aqueous phase was extracted several times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the solvent was removed. The residue was purified by chromatography on neutral aluminum oxide using toluene as eluent to yield 142 mg of the phosphinite borane **17**: yield = 85%; colorless crystals; mp = 68 °C; R_f = 0.6 (toluene); $[\alpha]^{20}_D$ = −19.2 (*c* 1.1, $CHCl_3$) for 97% ee; IR (ν cm^{-1}) 3060−2837 (CH), 2390, 2347, 1589, 1574, 1505, 1477, 1462, 1431, 1279, 1263, 1203, 1164, 1019, 904, 824, 757, 733, 693; ^1H NMR ($CDCl_3$) δ (ppm) 0.40−1.86 (3H, br), 2.24 (3H, s), 3.59 (3H, s), 6.86−7.97 (13H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 20.7 (s), 55.4 (s), 111.7 (s), 112.1 (d, J_{PC} = 4.8), 115−136, 150.6 (d, J_{PC} = 5), 161.5 (d, J_{PC} = 2.6); ^{31}P NMR ($CDCl_3$) δ (ppm) 108,72 (q, $^1J_{PB}$ = 74.4); MS (EI) *m*/*z* (relative intensity) 335 (M^+ − H; 100), 323 (66), 216 (29), 215 (99), 91 (85). Anal. Calcd

(27) Al-Masum, M.; Kumaraswamy, G.; Livinghouse, T. *J. Org. Chem.* **2000**, *65*, 4776−4778.

(28) Stoop, R.; Mezzetti, A.; Spindler, F. *Organometallics* **1998**, *17*, 668−675.

(29) Hideyuki, T.; Imamoto, T. *Synlett* **2001**, 999−1002.

(30) Dunina, V. V.; Kuz′mina, L. G.; Kazakova, M. Y.; Grishin, Y. K.; Veits, Y. A.; Kazakova, E. I. *Tetrahedron*: *Asymmetry* **1997**, *8*, 2537−2545.

(31) (a) Neetkoven, U.; Kamer, P. C. J.; van Leeuwen, Piet W. N. M.; Widhalm, M.; Spek, A. L.; Lutz, M. *J. Org. Chem.* **1999**, *64*, 3996−4004. (b) Ewalds, R.; Eggeling, E. B.; Hewat, A. C.; Kamer, P. C. J.; van Leeuwen, Piet W. N. M.; Vogt, D. *Chem. Eur. J.* **2000**, *6*, 1496−1504.

(32) Rippert, A. J.; Linden, A.; Hansen, H. J. *Helv. Chim. Acta* **2000**, *83*, 311−321.

for $C_{20}H_{22}BO_2P$ (336.1722): C, 71.46; H, 6.60; B, 3.22; P, 9.21. Found: C, 70.01; H, 6.51; B, 3.32; P, 9.15.

The enantiomeric excess and the absolute configuration of the *p*-tolyl phosphinite borane (*R*)-**17** were determined by HPLC analysis on a Chiracel OK Daicel column of the PAMP borane (*S*)-**12a**, resulting from reaction at low temperature (<−50 °C) with methyllithium.

(*S*,*S*)-(−)-1,2-Bis(methylphenylphosphinitoborane)-benzene 18. In a 50 mL two-necked flask equipped with a magnetic stirrer and an argon inlet was added 2.2 mmol of *sec*-butyllithium under stirring at 0 °C to a solution of catechol (1 mmol) in 2 mL of THF. After 1 h, THF was added to dissolve the catecholate, and the resulting solution was cooled to −78 °C. The catecholate was then added at −78 °C to a toluene solution of the chlorophosphine borane **4a** (3 mmol), previously prepared as described above. The resulting mixture was progressively warmed to 0 °C and stirred for 1 h. After hydrolysis with 5 mL of water, the aqueous phase was extracted several times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the solvents were removed. The residue was purified by chromatography on silica gel using toluene/petroleum ether 7:3 as eluent, yielding the phosphinite borane **18** in 86% yield: white crystals (CH_2Cl_2/hexane); mp = 135 °C; R_f = 0.45 (toluene); $[\alpha]^{20}_D$ = −64.5 (*c* 1.0, $CHCl_3$); IR (ν cm^{-1}) 3056−2918, 2410−2341, 1589, 1489, 1450, 1436, 1401, 1314, 1297, 1249, 1180, 1137, 1115, 1102, 1057, 1029, 905, 860, 799, 768, 743, 692; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.20−1.80 (6H, sl), 1.90 (6H, d, $^2J_{HP}$ = 8.8), 6.90 (4H, s), 7.40−7.70 (6H, m), 7.80−7.95 (4H, m); ^{13}C NMR ($CDCl_3$): δ(ppm) 16.5 (d, $^1J_{PC}$ = 44.1), 122.2 (d, J_{PC} = 4.2), 125.1, 129.0 (d, J_{PC} = 10.4), 131.2 (d, J_{PC} = 11.6), 131.3 (d, J_{PC} = 55.3), 132.8 (d, J_{PC} = 2.2), 143.6 (m); ^{31}P NMR ($CDCl_3$) δ(ppm) +119.4 (q, $^1J_{PB}$ = 55.7); MS (EI, 70 eV) *m*/*z* (relative intensity) 381 (M^+ − H; 5), 367 (M^+ − H − BH_3; 25), 243 (30), 227 (30), 217 (10), 149 (25), 139 (20), 123 (100); HRMS (DCI, CH_4) calcd for $C_{20}H_{25}B_2O_2P_2$ [M^+ − H] 381.1523, found 381.1541.

(*S*)−(−)-Methylphenyl-*S*-phenylthiophosphinite Borane 19. In a 50 mL two-necked flask equipped with a magnetic stirrer and an argon inlet was added 2.9 mmol of *n*-butyllithium under stirring at 0 °C to a solution of thiophenol (3 mmol) in 5 mL of THF. After 1 h, the thiophenolate was cooled to −78 °C. It was then added at −78 °C to a toluene solution of the chlorophosphine borane **4a** (2 mmol), previously prepared as described above. After an additional 1 h, the mixture was hydrolyzed by water (10 mL), and the aqueous phase was extracted several times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and the solvent was removed. The residue was purified by chromatography on silica gel using toluene as eluent, yielding the thiophosphinite borane **19** in 87% yield: white powder; mp = 66−69 °C; R_f = 0.65 (toluene); IR (ν cm^{-1}) 3077−3061, 2385−2337, 1475, 1438, 1109, 1050, 1024; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.30−1.70 (3H, br), 1.80 (3H, d, $^2J_{HP}$ = 8.9), 7.20−7.67 (10H, m); ^{13}C NMR ($CDCl_3$) δ (ppm) 13.7 (d, $^1J_{CP}$ = 32.9), 126.9 (d, J_{CP} = 5.2), 129.0 (d, J_{CP} = 10.3), 129.5 (d, J_{CP} = 1.7), 130.0 (d, J_{CP} = 2.3), 130.5 (d, $^1J_{CP}$ = 45.7), 131.9 (d, J_{CP} = 10.5), 132.3 (d, J_{CP} = 2.3), 136.6 (d, J_{CP} = 2.6); ^{31}P NMR ($CDCl_3$) δ (ppm) 47.7 (q, $^1J_{PB}$ = 56.4); MS (EI) *m*/*z* (relative intensity) 243 (M^+ − 3H; 30), 232 (M^+ − BH_3; 100), 217 (M^+ − BH_3 − CH_3; 50), 200 (25), 183 (12), 155 (12), 139 (17), 124 (60), 109 (22), 89 (22), 77 (72), 65 (42), 51 (57), 39 (37). Anal. Calcd for $C_{13}H_{16}BPS$ (246.115): C, 63.44; H, 6.55; B, 4.39; P, 12.59. Found: C, 62.23; H, 6.48; B, 4.50; P, 12.62.

The enantiomeric excess of the thiophosphinite borane **19** was determined by HPLC analysis on a Chiralcel OK Daicel column, eluent: hexane/ethanol 9:1, by comparison with a racemic sample: 1 mL/min, λ = 254 nm: (*S*)-**19**, t_R = 17 min; (*R*)-enantiomer, t_R = 21 min.

(+)-*N*,*N*′-Bis[(*R*)-*o*-Anisylphenylphosphinoborane]-ethylenediamine 20. In a two-necked flask, equipped with a magnetic stirrer and an argon inlet, 2.2 mmol (152 mg) of sodium hydride (60% in mineral oil) was washed twice with 2 mL of dry pentane and dissolved in 2 mL of anhydrous THF. Ethylenediamine (1 mmol, 67 μL) was then added. The resulting mixture was stirred at room temperature for 3.25 h. A solution of the chlorophosphine borane (3 mmol), freshly prepared following the previously described procedure, was cooled at −78 °C, and a solution of the freshly prepared dianion in 4 mL of dry THF was added dropwise. The mixture was allowed to warm to rt for 17 h. The reaction was hydrolyzed with 10 mL of water. THF was removed under reduced pressure, and the aqueous layer was extracted three times with dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvent was removed. The residue was purified by chromatography on silica gel, using a mixture of toluene/petroleum ether 7:3, followed by an 8:2 mixture, and finally toluene as eluent, to yield the bis-aminophosphine borane as a white solid which could be recrystallized from a CH_2Cl_2/hexane mixture: yield = 89%; white solid; R_f = 0.22 (toluene); $[\alpha]^{25}_D$ = +24.5 (*c* 1.0; $CHCl_3$); IR (KBr, ν cm^{-1}) 3353, 3329, 3065, 2969−2838, 2371, 1590, 1575, 1477, 1459, 1432, 1396, 1382, 1278, 1247, 1135, 1107, 1098, 1066, 1044, 1020, 881, 821, 800, 762, 746, 700, 688; ^{1}H NMR ($CDCl_3$) δ (ppm) 0.20−1.80 (6H, br), 3.00−3.30 (6H, m), 3.46 (6H, s), 6.75 (2H, dd, *J* = 3.1, 8.2), 6.96 (2H, m), 7.20−7.45 (12H, m), 7.86 (2H, ddd, *J* = 1.5, 7.5, 13.5); ^{13}C NMR ($CDCl_3$) δ (ppm) 44.7 (dd, *J* = 1.9, 6.8), 55.5, 111.2 (d, *J* = 4.0), 120.4 (d, J_{PC} = 58.7), 121.0 (d, *J* = 12.7), 128.0 (d, J_{PC} = 10.9), 130.1 (d, J_{PC} = 10.9), 130.1 (d, J_{PC} = 2.4), 133.5 (d, J_{PC} = 2.0),134.5 (d, $^1J_{PC}$ = 69.5), 134.7 (d, J_{PC} = 16.3), 160.7 (d, J_{PC} = 1.7); ^{31}P NMR ($CDCl_3$) δ (ppm) +55.29 (d, *J* = 80.8). Anal. Calcd for $C_{28}H_{36}N_2B_2P_2O_2$ (516.177): C, 65.15; H, 7.03; N, 5.43. Found: C, 65.04; H, 7.10; N, 5.43. The enantiomeric excess and the absolute configuration of the diaminophosphine borane **20** were determined by HPLC analysis on a Chiracel OK Daicel column of the PAMP borane (*R*)-**12b**, resulting from acid methanolysis[18,20] then reaction at low temperature (<−50 °C), with methyllithium.

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Supporting Information Available: Synthesis of the aminophosphine boranes **11a**−**h**. Structures and crystal data for the (S_P)-(+)-*N*-methyl[(1*R*,2*S*)(2-hydroxy-1-phenyl)ethyl]-amino-*tert*-butylphenylphosphine borane **11h**, (*R*)-*o*-anisylphenyl-*o*-tolylphosphine **14**, (*S*,*S*)-(−)-1,2-bis(methylphenylphosphinitoborane)benzene **18**, and (+)-*N*,*N*′-bis[(*R*)-*o*-anisylphenylphosphinoborane]ethylenediamine **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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